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Metal Finishing Industry Workshop (SIC 347)

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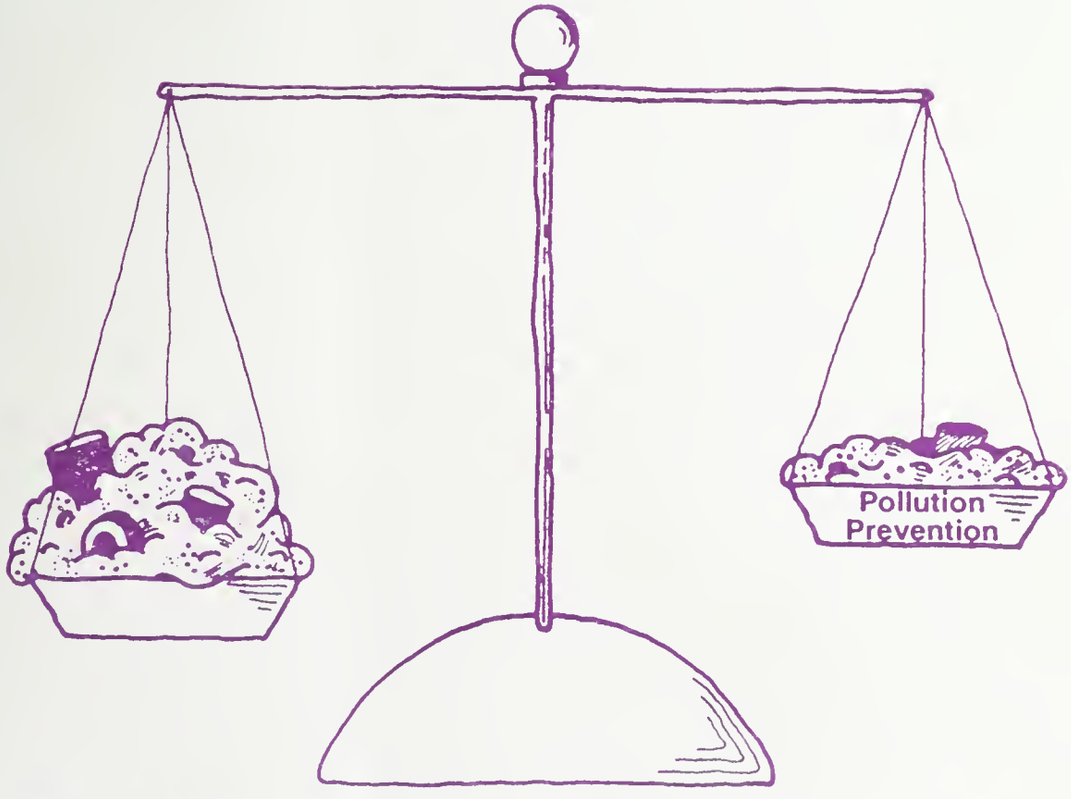

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Outline for IEPA Workshop on the Metal Finishing Industry

I. Introduction to the Metal Finishing Industry

A brief history of the metal finishing Industry and the evolution of metal finishing processes to their modern form.

II. Metal Finishing Process Overview

Basic Flow diagrams illustrating the flow of raw materials, products, and wastes. Processing sequence information for various metallic substrates.

III. Metal Finishing Process Details

Details of various metal finishing processes, including operating principles, by-products, and wastes generated.

IV. Recycling Methods Used in the Metal Finishing Industry

Information on the types of recycling methods available for use in the metal finishing industry.

V. Pollution Prevention Methods in the Metal Finishing Industry

Process modifications, pollution prevention planning, and substitution methods available for metal finishers.

VI. Statutory and Regulatory Obstacles to Pollution Prevention

Regulations and other requirements that can act as barriers to adoption of pollution prevention by the metal finishing industry.

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I. Introduction to the Metal Finishing Industry

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Part I, Introduction To The Metal Finishing Industry

METAL FINISHING
* Enhance the surface of metal
* Application of metallic coating
  * Protection from corrosion
  * Enhanced wear properties
  * Enhanced appearance

"Metal Finishing" is a generic term applied to a variety of processes for the purpose of enhancing one or more properties of the surface of a metal. It is also applied to a number of processes that involve the application of a metallic coating to a non-metallic surface such as plastic, ceramic, epoxy, and even baby shoes.

The art of creating an altered surface on a metallic substrate dates back to several centuries before Christ. Methods of metal finishing such as polishing, grinding, and painting were performed in the same era, along with non metal finishing processes such as heat treating and tempering of metals.

The modern metal finishing era, however, began with the invention of the galvanic cell in the early 1800's. By the middle of the 19th century, silver, gold, copper, and brass plating were commercially performed. In addition to electroplating, numerous competitive methods of altering the surface of metals and non-conductors have been added to the common definition of metal finishing since the 19th century.

Early metal finishing processes were focused on decorative endeavors such as jewelry and decorative items such as lamps and hardware. However, some massive parts were manufactured utilizing an electroplating method called "electro-forming", including the street lamp standards for the streets of Paris.

The metal finishing industry received a big boost from the advent of the industrial age, and the development of electricity generators in the late 1800s. Metal machine components, hardware, and automotive parts required protection from corrosion enhanced wear properties, and enhanced appearance.

World Wars I and II and the aircraft industry further developed and refined the industry by adding such processes as anodizing, conversion coating, chromium plating, bronze alloy plating, nickel plating, chemical milling and phosphating, along with numerous other plating processes. Plating equipment evolved from manually operated wooden process tanks to automated equipment, capable of processing thousands of pounds per hour of parts.

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METAL FINISHING TIME LINE

<---------0	1800	1850	1917---1945	1945----->	1969	1972	1977
I	Galvanic	I	Anodizing	Electro-paint	I	Water	I
I	Cell	I	Conv. Coating	Electroless Pltg	I	Pollution	I
Polishing		Silver	Chromium Pltg	Electropolishing	I	Control Act	I
Grinding		Gold	Bronze Alloy	Vacuum Metalizing	I		Clean
Painting		Copper	Nickel Pltg	Mech. Pltg	I		Water
Heat treat		Brass	Chem. Milling	Electrostatic paint	I		Act
Tempering		Plating	Phosphating	Electrolytic paint	I		
			Other	Powder coating	I		
					MSD		

The modern era of metal finishing arrived following World War II. Processes such as electro-painting, electroless plating, electropolishing, vacuum metallizing, mechanical plating, electrostatic painting, Electrolytic painting (E-coat), and powder coating.

The peak of the metal finishing era is believed to have occurred during the 1950-1960 decade, with approximately 6000 job shops providing plating services and an unknown number of large manufacturers (such as Sunbeam, General Electric, and Westinghouse) employing metal finishing facilities as part of their manufacturing processes.

Until 1972, the metal finishing industry was environmentally unregulated (except for selected areas such as Chicago, where a local ordinance by the Metropolitan Sanitary District was passed in 1969) and discharges of concentrated chemicals from metal finishing processes to sewer systems and surface waters was common. In 1972, Congress gave the Environmental Protection Agency (USEPA) the authority to create regulations for industrial dischargers to the surface waters of the USA, under the Water Pollution Control Act (Public Law 92-500). In 1977, Congress gave EPA additional powers to regulate discharges to sewers under the "Clean Water Act (Public Law 95-217). Under this mandate from Congress, EPA developed a system of "categorizing" all industries that discharged pollutants to the surface waters and sewers of the USA. EPA then passed regulations limiting the concentrations and amounts of pollutants that could be in the discharges of process water from those categorical industries. EPA also studied and provided technical information on what technologies could be employed to comply with their regulations.

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DIRECT DISCHARGERS:

- NPDES PERMIT
- TOXIC POLLUTANTS
- CONVENTIONAL POLLUTANTS
- TECHNOLOGY:
  - Precipitation
  - Clarification
  - CN-Destruct
  - Cr-reduction
  - Oil Removal
  - Precious Metals Recovery

EPA realized that the most serious threat to the environment arose from facilities that discharged directly into the rivers (navigable waters such as lakes, bays, rivers, creeks, and most all other surface waters down to very small rivulets). They, therefore, first passed regulations on those discharges and thereby created the National Pollutant Discharge Elimination System (NPDES). Under this system, an NPDES permit is issued to each direct discharger. This permit specifies the maximum concentration of each pollutant in addition to such things as BOD (Biochemical Oxygen Demand), TDS (Total Dissolved Solids), FOG (Fats, Oils, and Greases), and numerous other "conventional" pollutants (pollutants that are not toxic and are normally assimilated by the receiving stream, but can significantly affect the quality of the receiving stream).

NPDES discharge limits are based on BAT/BPT - that is the best practicable control technology presently available. The technology used for compliance purposes includes "precipitation of metals and clarification plus cyanide destruction, reduction of hexavalent chromium to trivalent, oily waste separation, precious metals recovery, and total toxic organics (TTO) control". Note that most discharge regulations are concentration based (usually measured in mg/L). Some specific regulations allow the option of mass based standards (measured in mg/Kg of parts processed).

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40CFR parts 400-424

40CFR part 413 Electroplating
Point Source Category

40 CFR part 433 Metal Finishing
Point Source Category

Subparts A: Common Metals
B: Precious Metals
C: Specialty Metals
D: Anodizing
E: Coatings
F: Chemical Etching/ Milling
G: Electroless Plating
H: Printed Circuit Board

There are now discharge regulations covering every source of metal finishing wastewater. These can be found in the "Code of Federal Regulations" (40CFR) parts 400 to 424 and parts 425 to 629. A job shop electroplating company that existed prior to August 8, 1981, (a job shop is one that processes at least 51% of parts that are owned by others), is regulated per part 413 of 40CFR. Note that part 413 is divided into Subparts A through H and each subpart may have different regulations. If the company has a single discharge but performs multiple processes under various subparts, then the most stringent of the differing regulations apply. A job shop electroplating Company that came into existence after August 8, 1981 is considered a new source metal finisher and is regulated under section 433 of 40CFR.

The "metal finishing industry" covered so far, has been a "generic", commonly used reference. However, EPA created a legal definition of what activities constitute metal finishing under the Clean Water Act of 1977 (published Feb. 28, 1981). A company falls into the metal finishing category under the following circumstances:

If the company processes fewer than 50% (based on surface area) of parts that are owned by others **and** performs any one of the following processes: Electroplating, Electroless Plating, Anodizing, Coating (chromating, phosphating, coloring), chemical etching & milling or Printed Circuit Board Manufacture, the metal finishing regulations apply to the wastewater discharges from these operations **and** from any of the 45 operations listed in Table 1.

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TABLE 1

AUXILLIARY PROCESSES REGULATED UNDER METAL FINISHING IF ONE OR MORE OF THE SIX PRIMARY METAL FINISHING OPERATIONS IS PERFORMED.

Cleaning
Machining
Grinding
Polishing
Tumbling
Burnishing
Impact Deformation
Pressure Deformation
Shearing
Heat Treating
Thermal Cutting
Welding
Brazing
Soldering
Flame Spraying
Sand Blasting
Other Abrasive Jet Machining
Electric Discharge Machining
Electrochemical Machining
Electron Beam Machining
Laser Beam Machining
Plasma Arc Machining
Ultrasonic Machining
Sintering
Laminating
Hot Dip Coating
Sputtering
Vapor Plating
Thermal Infusion
Salt Bath Descaling
Solvent Degreasing
Paint Stripping
Painting
Electrostatic Painting
Electropainting
Vacuum Metallizing
Assembly
Calibration
Testing
Mechanical Plating

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Job shop electroplating companies formed after August 8, 1981 and existing job shops that re-locate or massively alter their existing shops, are also categorized as "metal finishers" for purposes or regulation under the Clean Water Act.

For the balance of this introduction, we shall assume the "generic" definition of metal finishing.

Following regulation under the Clean Water Act, the industry was deluged by regulations under numerous other "Acts", including RCRA (Resource Conservation and Recovery Act), Clean Air Act, SARA (Superfund Amendments and Reauthorization Act), CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act), EPCRA (Emergency Planning and Community Right to Know Act), and OSHA (Occupational Safety and Health Act).

With few exceptions, each of these regulations seriously impacted the metal finishing industry and caused it to "evolve" in response.

CLEAN WATER ACT - Pretreatment systems for removal prior to discharge
RCRA - Treat & dispose of wastes in environmentally sound manner
CERCLA/SARA - Cautious waste disposal - where & whom
EPCRA - Review & Reduce hazardous chemicals
OSHA - Protect workers from chemical exposures

The Clean Water Act caused the industry to install and operate pretreatment systems for the removal of heavy metals and other toxins such as cyanide, prior to discharge. Because these pretreatment systems were sized and priced based on volume, the industry investigated and employed water conservation methods such as drag-out rinsing and counterflow rinsing.

RCRA required the industry to treat and dispose of wastes generated from metal finishing operations and pretreatment systems in an environmentally sound manner. The industry responded by developing alternate processes that generated less waste or waste that was less toxic or non-hazardous.

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CERCLA/SARA caused the industry to become much more cautious about where and whom to send there wastes for disposal.

EPCRA caused the industry to review and reduce the quantities of hazardous chemicals on hand at any given time, reducing potential danger to their neighbors.

OSHA regulations have caused the industry to change to less toxic processes and to ventilate their processes in order to protect their workers from chemical exposures.

Common Metal Finishing Operations

Today, in addition to between 12,000 and 30,000 captive metal finishing facilities, there are approximately 3,000 job shop electroplating companies. They are considered to be a "service" industry, in that they take parts manufactured by others, apply a metal finishing process or processes to those parts, and then return them to their client.

Of the 45 processes in Table 1, the following are the most commonly applied metal finishing operations:

COMMON METAL FINISHING OPERATIONS:

Electroplating
Electroless Plating
Anodizing
Phosphating
Conversion Coating
Burnishing
Electropolishing
Chemical Milling/Etching
Electropainting
Vacuum Metallizing
Mechanical Plating
Spray Painting
Powder Coating

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	Chemical Solution	DC Current	Reducing Agent	Cost	Complex Uniform Coverage
Electroplating	X	X		Low	No
Electroless Plating	X		X	High	Yes

Electroplating is the most commonly applied metal finishing process. It utilizes a combination of a chemical solution formulated to contain metal ions or complexed metal ions plus a DC electric current to convert the metal ions in solution to solid metal atoms on the surface of the substrate that the DC current is applied to. Electroplating offers the advantages of being inexpensive, requiring relatively inexpensive equipment, comparatively easy and safe to do, and easy to do in bulk quantity. Plated metal coatings can be used for a variety of purposes, including corrosion resistance, appearance, solderability, electrical resistance, electrical conductivity, vibratory bonding, abrasion resistance, electro-forming of a product, and as a matrix to hold abrasives such as diamonds and carbides in cutting tools. By far, the widest variety of metal surface properties can be obtained through electroplating processes.

Electroless Plating utilizes a chemical solution containing metallic ions, but no DC current is applied. The "electrons" required for reducing metal ions to metal atoms are instead supplied by another chemical ingredient, called a "reducing agent". Electroless plating is very expensive, more dangerous to perform, and difficult to do in bulk quantity. Equipment costs are similar. Electroless plating offers the advantage of providing very uniform coverage over complex shapes, while electroplating can not cover complex shapes uniformly, without use of labor consuming shields and auxiliary anodes. Electroless plating processes can also provide coatings with unique properties such as magnetism, corrosion resistance and abrasion resistance. Electroless plating processes are commonly employed in the manufacture of electronic components and printed circuit boards (properly termed printed wiring boards).

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CONVERSION COATINGS

Anodizing

* Applied to Al and Mg
* Chemical Solution (no metal ions), DC current (+)
* Converts surface to an oxide, dissolved

Anodizing is a process most commonly applied to aluminum and magnesium. The process utilizes a chemical solution and DC current to convert the surface of the metal parts to an oxide, commonly called an anodized coating. The process differs from electroplating in that the process solution does not contain metal ions and the coating is not **applied** to the surface. The surface is actually simultaneously converted to the oxide and dissolved by the chemical solution, creating billions of tiny pores in the coating, which allow the coating to be colorized using dyes and other specialized techniques. During anodizing, the aluminum or magnesium parts have a positive (+) DC charge applied, while in electroplating, the parts are negatively (-) charged.

CONVERSION COATINGS

Phosphating

* Converts surface into crystalline phosphate coating
* 3 Categories: Iron - Spray, prior to painting
  Zinc - Steel, prior to oil
  Manganese - Thick, abrasion resistant

Phosphating is another "conversion" process, that utilizes an acidic solution containing phosphoric acid and other ingredients to convert the surface of the steel parts into crystalline phosphate coatings. There are three major categories of phosphates, iron, zinc, and manganese. Iron phosphates are most commonly applied in spray operations prior to painting, in equipment typically termed a phosphating line. Zinc phosphate can also be applied prior to painting, but is commonly applied to steel parts (especially fasteners such as machine screws and bolts) prior to application of a corrosion inhibiting oil. The phosphate crystals act as a holding mesh for the oil. Manganese phosphates are very thick, abrasion resistant coatings applied to specialized parts in the aerospace industry and on hardware subjected to an abrasive environment.

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Other Conversion Coatings

* Black Oxide - Sodium Hydroxide, high temp.
* Chromating - Chromates & other chemicals, thin film
* Coloring - Chemicals convert surface to desired color

Conversion Coating is a generic term for any process that converts the surface of a part to a coating. We have just covered two conversion coatings that are somewhat specialized (anodizing and phosphating), but there are numerous other types of conversion coatings:

Black Oxide: An immersion process in which metal parts are immersed in a molten solution of sodium hydroxide at high temperature (275 °F) to form a black iron oxide.

Chromating: An immersion process in which metal parts are immersed in a solution containing chromates and other chemicals for the purpose of converting the surface to a thin film that enhances the corrosion resistance and paint adhesion of the surface.

Coloring: An immersion process that utilizes chemicals to convert the surface of a metal part to a coating that has a desired color. This process is commonly employed by decorative lamp, furniture and hardware manufacturers.

Burnishing: Water solution with abrasive - vibrated or tumbled

Electropolishing: Chemical Solution & DC current - mirror smooth surface

Chemical Milling/Etching: Chemical solution dissolves unmasked area

Burnishing is a process that utilizes a water solution of soaps and other ingredients along with abrasive media to remove sharp edges and metal slivers from stampings and machined/drilled parts. The parts are vibrated or tumbled with this mixture until the desired finish is obtained.

Electropolishing utilized chemical solutions and DC current to dissolve off a thin film of metal from a surface in such manner that more metal is removed from the peaks of rough surfaces than from the valleys. The resulting surface can be mirror smooth. The process is most commonly applied to stainless steel components, especially in the food

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service and medical industries, for appearance and because an electropolished surface inhibits bacterial growth.

Chemical Milling/Etching are processes commonly employed in the aerospace industry and in the manufacture of printed wiring boards. The metal parts are masked with a chemical resistive coating at areas that are not to be etched/milled, and are then immersed in a chemical solution that dissolves the unmasked area at a uniform rate, until the desired amount of metal is removed.

Electropainting: DC current and specialized paint

Vacuum Metallizing: Vaporized metal ions, vacuum chamber

Mechanical Plating: Tumbling of solution, metallic powder & glass beads

Spray Painting: Solvent or water based, possible charge

Powder Coating: High temp, eliminates solvents

Electropainting utilizes DC current and a specialized paint that becomes adherent to immersed metal parts, when the current is applied. The combination of current and paint allows for more uniform and complete coating of complexed shaped parts. The process is commonly performed by the automotive industry on car body panels and on hardware.

Vacuum Metallizing is a process that utilized vaporized metal ions in a vacuum chamber that "condense" onto the parts held within the chamber and thus metallize the parts (along with everything else inside the chamber). The process is commonly employed to apply thin metallic films on plastic parts such as toys. Variations of the process are also currently in use to apply thick coatings of aluminum, cadmium, titanium nitride and numerous other coatings on industrial parts, inexpensive jewelry, and aircraft components. The process is almost pollution free, but the equipment is very expensive and limited in productivity.

Mechanical Plating utilizes water based solutions containing various patented ingredients, plus metallic powder and glass beads. The solution and parts to be coated are tumbled in large rotary tumblers. As the beads and parts impact with each other, the metallic powder is "hammered" into the surface of the parts, creating a coating of the metal powder. The process avoids the use of more hazardous chemicals as in electroplating and does not cause hydrogen embrittling effects on high strength steel, but is limited in appearance and the types/combinations of coatings that can be applied.

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Spray Painting is applied to numerous consumer products utilizing a painting line that may include a phosphating operation prior to painting. The parts are sprayed with various paints that may contain solvents or may be water based. Spray painting may be accomplished with the use of an electrostatic charge applied to the parts in order to attract the paint to recessed areas and created more efficient use of the paint.

Powder Coating utilized specialized powders that melt onto the parts when heated to a high temperature, thereby creating the "painted" coating. Use of powder eliminates the solvents used in conventional spray painting operations and can created very thick, highly corrosion resistant coatings. Parts must be able to withstand the high temperatures of the baking of the powder (325 °F or more), however.

METAL FINISHING PROCESSES

* Part Preparation: Creates rinsewater and spent chemicals
* The Process: Generates wastes, spent solutions, by-products
* After processing: Additional chemical operations, stripping, rejects
* Equipment: Scrubbing, ventilation, filtration

A modern metal finishing facility may utilize one or more of the above processes to conduct their business. Each process will require the parts to be prepared prior to the application of the process. Such preparation usually utilizes cleaning and pickling chemicals and rinses, creating rinsewater and spent chemicals. The process itself will normally generate wastes and spent solutions or by-products. After processing, there may be additional chemical operations and there also may be stripping operations to handle rejects. The equipment used to process the parts may require ventilation and scrubbing of exhaust air, resulting in additional waste generation from the scrubbing equipment and from maintenance of the ventilation equipment. The process solutions may require filtration equipment to remove particulates that can contaminate the processed surface. The filtration equipment can also generate waste.

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PART II, Metal Finishing Process Overview

METAL FINISHING FACILITIES
* Varying unit operations
* Variety of raw materials, chemicals used
* Variety of wastes generated

A metal finishing facility will consist of numerous unit operations, each designed to modify the surface or shape of a substrate in sequential order, up to the final process prior to packaging. Depending on whether the facility is a wholly owned department of a larger manufacturing company, or if it is a job shop working on parts owned by others, each facility will have a varying number of these unit operations. Since there are many ways to accomplish the same task, each facility may also employ different technologies in their unit operations. The result is a wide variety of operations, chemicals, and wastes generated. The following are simplified examples:

A. Metal Finishing Facilities: Case Studies

Example 1, Company Manufacturing Decorative Lamps.

OPERATION	RAW MATERIALS	WASTES
Casting	Solid Metal Alloy	Clean-Up Fluids
De-flashing	NONE	Metal Cuttings
Grinding	Grinding Wheels Castings	Metal Fines
Polishing	Polishing Wheels Castings Buffing Materials	Exhaust Dust
Vapor Degreasing	Chlorinated Solvent	Spent Solvent/Oil
Soak Cleaning	Alkaline Aqueous Cleaner Water	Spent Cleaner Oil/Grease Solid Sludge Waste Rinsewater
Electrocleaning	Alkaline Aqueous Cleaner Water	Spent Cleaner Oil/Grease Solid Sludge Waste Rinsewater

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Example 1, continued

OPERATION	RAW MATERIALS	WASTES
Acid Dip	Sulfuric Acid Water	Spent Acid Waste Rinsewater
Copper Strike	Copper Cyanide Sodium Cyanide Sodium Carbonate	Waste Rinsewater Filter Residuals Cyanide/Carbonate Solids
Nickel Plate	Nickel Sulfate Nickel Chloride Boric Acid Organic Additives	Waste Rinsewater Filtration Residuals Purification Residuals
Brass Plate	Copper Cyanide Zinc Cyanide Sodium Cyanide Organic Additives	Waste Rinsewater Filter Residuals Cyanide/Carbonate Solids
Stain	Various Staining Chemicals Such As Ammonium Polysulfide	Spent Stain Solution
Buff	Buffing Wheels Buffing Tallows	Buff Dust
Vapor Degreasing	Chlorinated Solvent	Spent Solvent/Oil
Lacquer	Lacquer Thinning Solvents	Lacquer Residuals Spray Booth Waste
Stripping of Rejects	Alkaline Stripping Chemicals	Spent Stripper

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Example 2, Manufacturer of Plated Steel Hardware

OPERATION	RAW MATERIALS	WASTES
Machine, Forge, Broach Raw Steel	Cutting Fluids Steel Rod/Sheet	Waste Cutting Fluids Metal Fines
Vibratory Finish	Water Soap Abrasive Media	Spent Vibratory Solution
Soak Cleaning	Alkaline Aqueous Cleaner Water	Spent Cleaner Oil/Grease Solid Sludge Waste Rinsewater
Electrocleaning	Alkaline Aqueous Cleaner Water	Spent Cleaner Oil/Grease Solid Sludge Waste Rinsewater
Acid Dip	Sulfuric Acid Water	Spent Acid Waste Rinsewater
Zinc Plate	Zinc Cyanide Sodium Cyanide Sodium Carbonate	Cyanide/Carbonate Sludge Waste Rinsewater Sludge/Solids
Chromate	Various Chromating Chemicals, Most Contain Hexavalent Chromium Compounds	Spent Chromate Solution Waste Rinsewater

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Example 3, Printed Wiring Board Manufacturer

OPERATION	RAW MATERIALS	WASTES
Clean Laminate	Cooper Laminated Epoxy Sheet Cleaner Water	Spent Cleaner
Drill registration Holes	Copper Laminated Epoxy Sheet	Copper/Epoxy Drillings
Apply Photoresist/Expose	Photo-resist	Plastic film
Etch	Copper Etching Solution (Typically Ammonium Persulfate)	Waste Etchant Rinsewater
Strip Photoresist	Alkaline Stripper Water	Spent Stripper And Rinsewater
Adhesion Promotion (for multi-layer boards)	Chromium-bearing rinses (Alternates: copper oxide solution or zinc or brass plating)	Spent solution and Rinsewater
Lamination	None	None
Drill holes	None	Copper/Epoxy Drillings
Etchback	Concentrated Acid or Alkaline/Permanganate (Unless plasma is used)	Spent Etchback Solution (Unless plasma is used)
Electroless Copper Plate	Copper Sulfate Fomaldehyde Complexing Agents Water	Spent Plating Solution Rinse Water
Copper Plate	Copper Sulfate Water Sulfuric Acid	Rinsewater Excess Plating Solution Contaminated Filter Media
Apply Photoresist/Expose	Organic Maskant Material	Plastic Film
Overplate (tin-lead)	Lead Fluoborate Tin Fluoborate Fluoboric Acid Water	Rinsewater Contaminated Carbon (from periodic treatment)

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Example 3 continued

OPERATION	RAW MATERIALS	WASTES
Strip Photoresist	Alkaline Stripper Water	Spent Stripper And Rinsewater
Etch	Copper Etching Solution (Typically Ammonium Persulfate)	Waste Etchant Rinsewater
Solder Reflow	None	None
Selective Solder Strip	Acid Stripping Solution Water	Spent Stripper
Selective Nickel Plate	Nickel Sulfate Nickel Chloride Boric Acid Organic Additives Water	Rinsewater Filtration Media Contaminated carbon
Selective Gold Plate	Potassium Gold Cyanide Additive Salts Water	Contaminated Ion Exchange Resin (sent for reclaim)
Final Drilling/machining of groves/slots	None	Copper/Epoxy Fines (May also contain tin and lead)

Note: there are many variations on the manufacturing process for printed wiring boards, only the basic steps are covered. Some operations may skip one or more of these steps or use alternate means.

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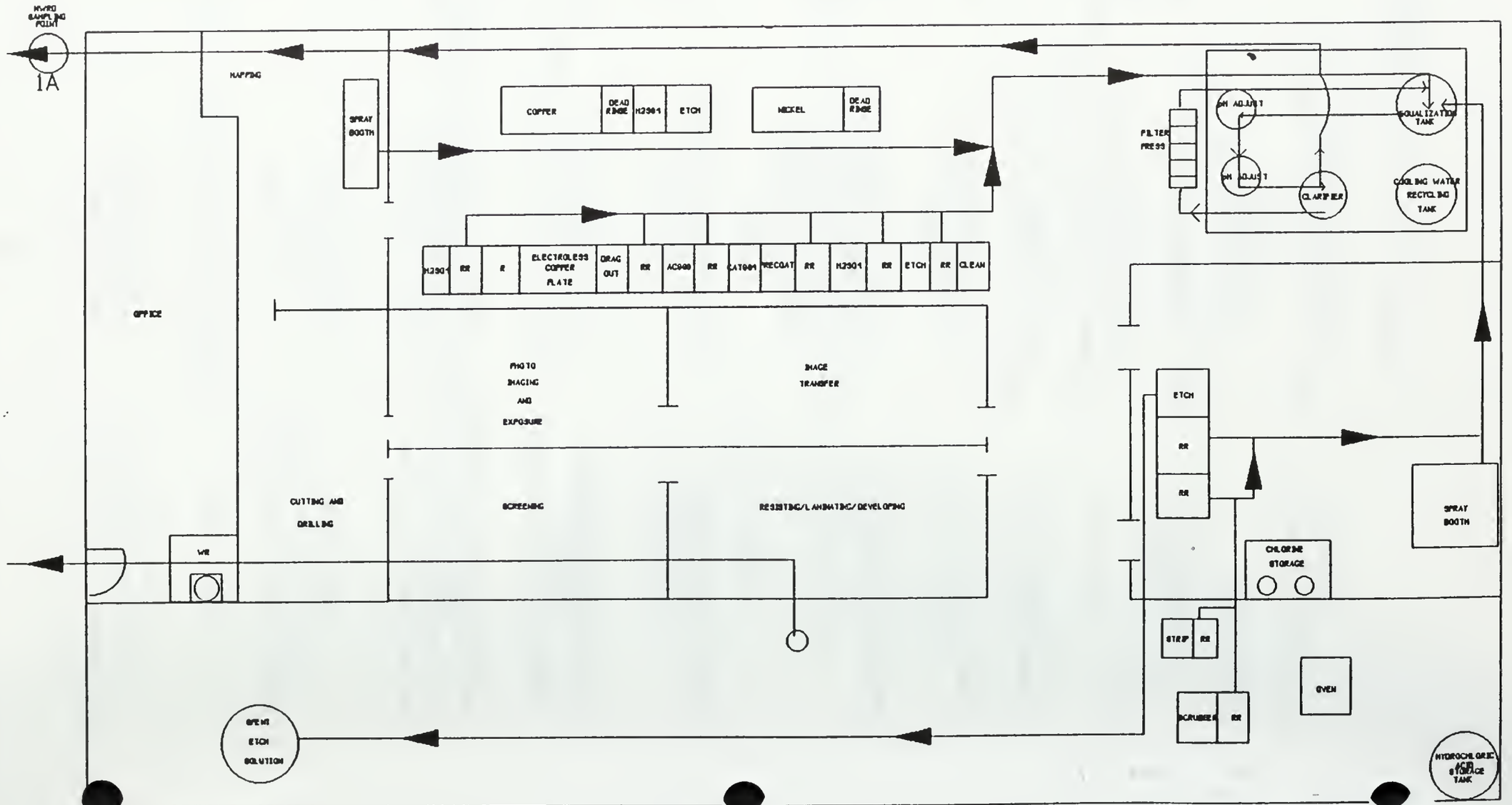
II Metal Finishing Process Overview

Cu^{+1} ● → ● Cu^{0}

Process Diagram, Printed Wiring Board Facility



Example 4, Small Job Shop Electroplater

OPERATION	RAW MATERIALS	WASTES
Soak Cleaning	Alkaline Aqueous Cleaner Water	Spent Cleaner Oil/Grease Solid Sludge Waste Rinsewater
Electroclean	Alkaline Aqueous Cleaner Water	Spent Cleaner Oil/Grease Solid Sludge Waste Rinsewater
Acid Dip	Sulfuric Acid Water	Spent Acid Waste Rinsewater
Zinc Plate	Zinc Cyanide Sodium Cyanide Sodium Carbonate	Cyanide/Carbonate Sludge Waste Rinsewater Sludge/Solids
Chromate	Various Chromating Chemicals, Most Contain Hexavalent Chromium Compounds	Spent Chromate Solution Waste Rinsewater
Apply Polyseal	Proprietary Seal (Organic Material)	Clean-up And Stripping Waste

B. KEYS TO SUCCESSFUL ELECTROPLATING

Keys To Successful Electroplating:

* Customized pre-plate cycle
* Knowledge of metallurgy
* Knowledge of substrate condition

The above examples illustrate that the bulk of wastes and of hazardous wastes are generated from the electroplating operation and the operations ancillary to electroplating. The types of wastes generated depend upon the metals/alloys to be electroplated and the types of metals plated onto the substrate(s).

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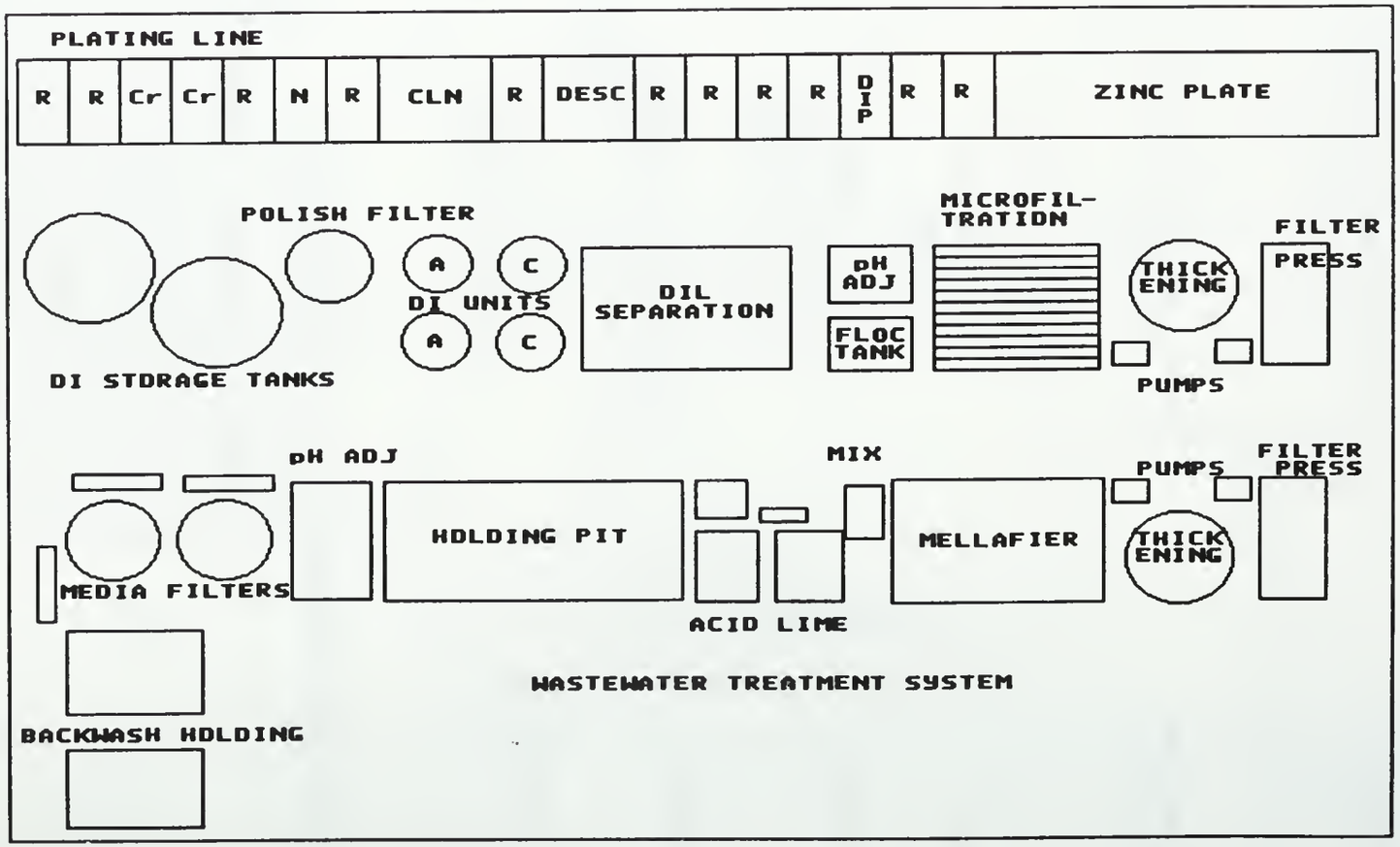
II Metal Finishing Process Overview

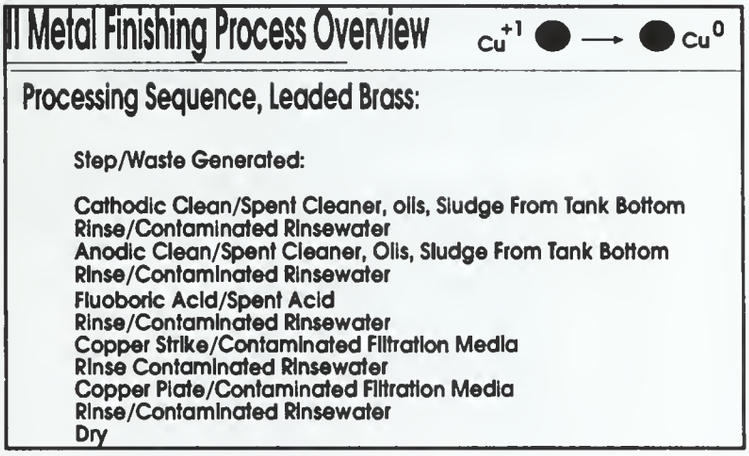
Cu^{+1} ● → ● Cu^{0}

Process Diagram, Small Job Shop Plating Facility

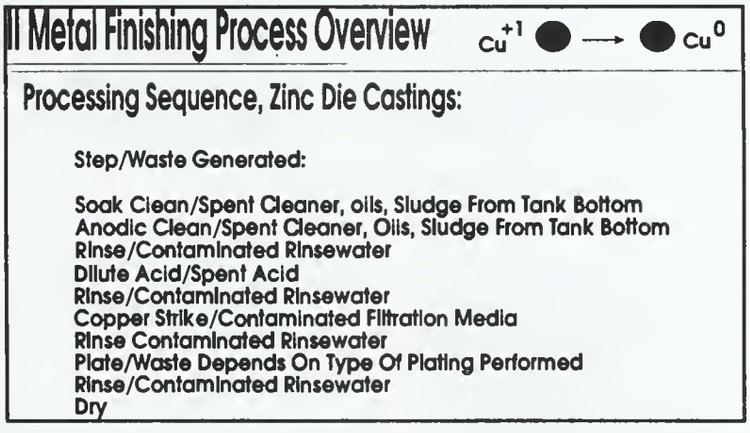


Before any part can be electroplated it must be properly "prepared". In fact, the "secret" to being a successful electroplater is in the knowledge of how to clean and prepare a substrate for plating. An improperly prepared substrate typically results in poor adhesion of the plated metal, resulting in peeling and or blistering. When properly prepared, the plated metallic layer will have about the same adhesion to the substrate as the individual metal atoms within the substrate have to themselves). There are some exceptions to this, notably plated metals on plastics, and metals that have a perpetual layer of tenacious oxide, such as aluminum, magnesium, titanium and stainless steels. Preparing the part for plating is typically performed in a series of tanks and rinses referred to as the "pre-plate cycle".

The preplate cycle typically is customized to the type of substrate that is to be plated. It may involve degreasing the part, then cleaning and acid pickling it, or it may be far more complicated. The following are common process steps used to electroplate different types of metal surfaces (vapor degrease is not included, but may be required). Note that wherever a new processing step (not covered above) is indicated, additional waste is generated in the form of spent solution and rinsewater:



Note: For non leaded brass and copper or copper alloys, substitute acid salts or sulfuric acid for fluoboric acid.



Note: A high pH nickel plate may be an alternate to the cyanide copper strike, but may pose some operational problems.

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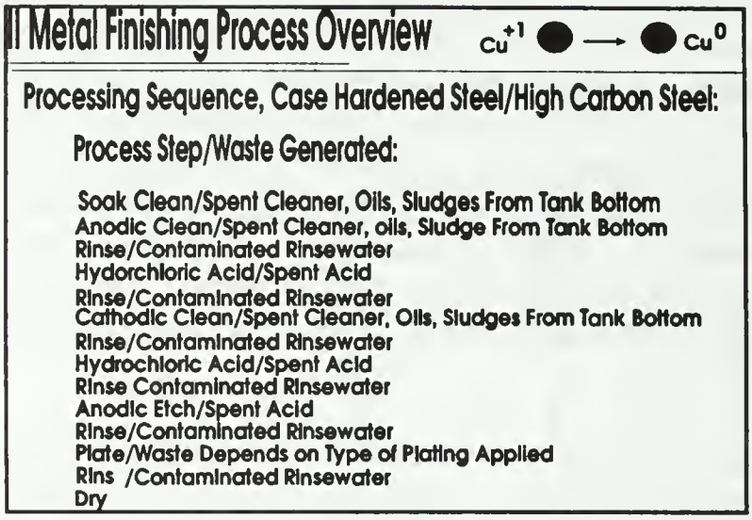
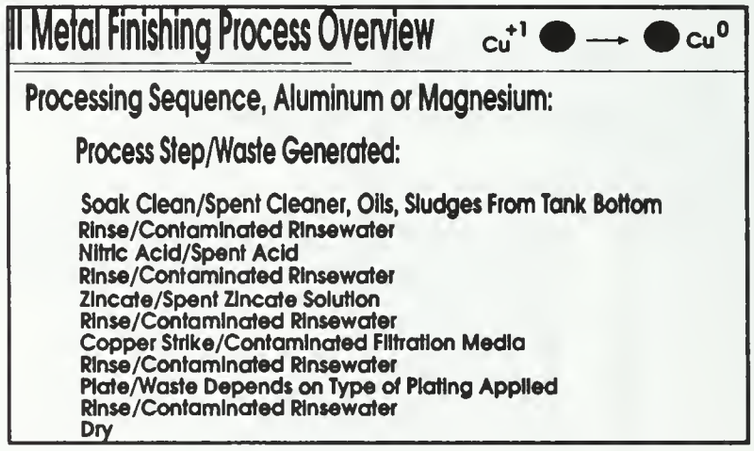

II Metal Finishing Process Overview
Cu+1 ● → ● Cu0
Processing Sequence, Case Hardened Steel/High Carbon Steel:
Process Step/Waste Generated:
Soak Clean/Spent Cleaner, Oils, Sludges From Tank Bottom
Anodic Clean/Spent Cleaner, oils, Sludge From Tank Bottom
Rinse/Contaminated Rinsewater
Hydorchloric Acid/Spent Acid
Rinse/Contaminated Rinsewater
Cathodic Clean/Spent Cleaner, Oils, Sludges From Tank Bottom
Rinse/Contaminated Rinsewater
Hydrochloric Acid/Spent Acid
Rinse Contaminated Rinsewater
Anodic Etch/Spent Acid
Rinse/Contaminated Rinsewater
Plate/Waste Depends on Type of Plating Applied
Rins /Contaminated Rinsewater
Dry

Note: Woods nickel strike may be substituted for Anodic Etch (Woods Nickel strike contains 250 g/L Nickel chloride plus 125 ml/L hydrochloric acid,)



Notes: Add bifluoride salts to nitric if the aluminum alloy contains silicon. If the parts are magnesium, substitute a solution of 10% Ammonium bifluoride in 20% phosphoric acid for the nitric acid, and substitute a pyrophosphate zincate for the normal zincate. Pyrophosphate zincate contains 1-1.6 oz/gal zinc sulfate plus 10-12 oz/gal sodium pyrophosphate. The bath operates at 170-180 deg. F, and the immersion coating forms in 3-5 minutes.

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II Metal Finishing Process Overview Cu^{+1} ● → ● Cu^{0}

Processing Sequence, 400 Series Stainless,Inconel, Hastelloy:

Process Step/Waste Generated:

Soak Clean/Spent Cleaner, Oils, Sludges From Tank Bottom
Rinse/Contaminated Rinsewater
Cathodic Clean/Spent Cleaner, Oils, Sludges From Tank Bottom
Rinse/Contaminated Rinsewater
Hydrochloric Acid/Spent Acid
Rinse/Contaminated Rinsewater
Anodic Wood's Nickel Strike/Contaminated Filtration Media
Rinse/Contaminated Rinsewater
Cathodic Wood's Nickel Strike/Contaminated Filtration Media
Rinse/Contaminated Rinsewater
Plate/Waste Depends on Type of Plating Applied
Rinse/Contaminated Rinsewater
Dry

II Metal Finishing Process Overview Cu^{+1} ● → ● Cu^{0}

Processing Sequence, 300 Series Stainless,Monel, Tool Steels:

Process Step/Waste Generated:

Soak Clean/Spent Cleaner, Oils, Sludges From Tank Bottom
Rinse/Contaminated Rinsewater
Cathodic Clean/Spent Cleaner, Oils, Sludges From Tank Bottom
Rinse/Contaminated Rinsewater
Hydrochloric Acid/Spent Acid
Rinse/Contaminated Rinsewater
Anodic in 25% Sulfuric Acid/Spent Acid
Rinse/Contaminated Rinsewater
Cathodic Wood's Nickel Strike/Contaminated Filtration Media
Rinse/Contaminated Rinsewater
Plate/Waste Depends on Type of Plating Applied
Rinse/Contaminated Rinsewater
Dry

II Metal Finishing Process Overview Cu^{+1} ● → ● Cu^{0}

Processing Sequence, Beryllium/Tellurium Copper:

Process Step/Waste Generated:

Soak Clean/Spent Cleaner, Oils, Sludges From Tank Bottom
Rinse/Contaminated Rinsewater
Sulfuric-Nitric Bright Dip/Spent Acid
Rinse/Contaminated Rinsewater
Hydrochloric Acid (50%)/Spent Acid
Rinse/Contaminated Rinsewater
Ammonium Persulfate/Spent Solution
Rinse/Contaminated Rinsewater
Copper Strike/Contaminated Filtration Media
Rinse/Contaminated Rinsewater
Plate/Waste Depends on Type of Plating Applied
Rinse/Contaminated Rinsewater
Dry

Note: brite dip: 2 gal Sulfuric Acid plus 1 gal Nitric Acid plus 1/2 fl oz Hydrochloric acid, No Water. Optional substitute: 20-30 % Sulfuric acid at 160-180 deg F.

II Metal Finishing Process Overview Cu^{+1} ● → ● Cu^{0}

Processing Sequence, Bronzes:

Process Step/Waste Generated:

Soak Clean/Spent Cleaner, Oils, Sludges From Tank Bottom
Rinse/Contaminated Rinsewater
Cathodic Clean/Spent Cleaner, Oils, Sludges From Tank Bottom
Rinse/Contaminated Rinsewater
Hydrochloric Acid (15%)/Spent Acid
Rinse/Contaminated Rinsewater
Nitric Acid (75%)/Spent Acid
Rinse/Contaminated Rinsewater
Copper Strike/Contaminated Filtration Media
Rinse/Contaminated Rinsewater
Plate/Waste Depends on Type of Plating Applied
Rinse/Contaminated Rinsewater
Dry

II Metal Finishing Process Overview Cu^{+1} ● → ● Cu^{0}

Processing Sequence, Titanium:

Process Step/Waste Generated:

Blast Clean/Contaminated Blasting Media
Hydrochloric Acid (20%)/Spent Acid
Rinse/Contaminated Rinsewater
Electroless Nickel Plate/Spent Plating Solution/Nitric Acid Waste
Rinse/Contaminated Rinsewater
Nickel Plate/Contaminated Filtration Media
Rinse/Contaminated Rinsewater
Diffuse/None
Sulfuric Acid (25%)/Spent Acid
Rinse/Contaminated Rinsewater
Plate/Waste Depends on Type of Plating Applied
Rinse/Contaminated Rinsewater
Dry

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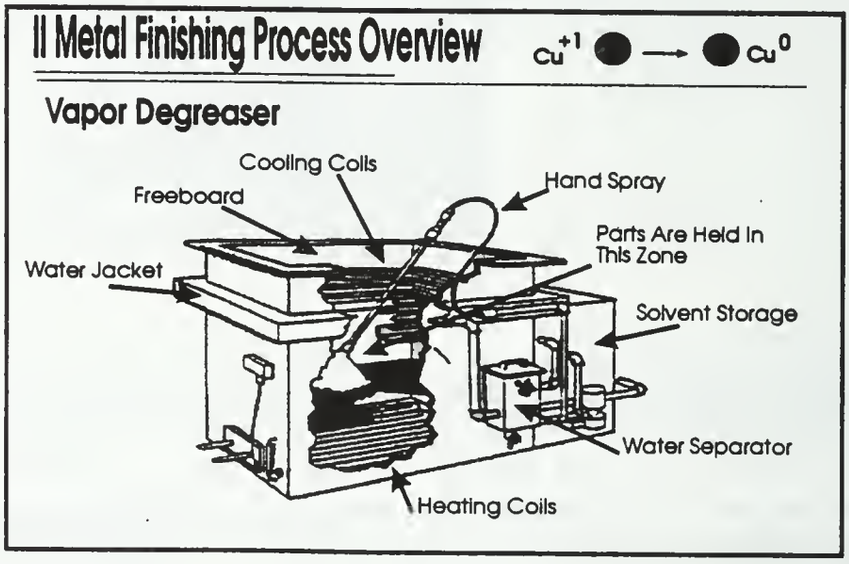
C. Process Step Details

The following are details of commonly employed processing steps indicated above:

1. PRE-CLEANING - to avoid solution contamination and obtain coating adhesion
   - A. Vapor degreasing
   - B. Pickling/ Descaling/Blasting
   - C. Soak Cleaning

1. PRE-CLEANING

Most metal parts are covered with grease or oil during their manufacture, by operations such as stamping, drilling, forging, buffing, and polishing. Heat treated steel parts may have a "scale" of iron oxides (rust) that would interfere with the appearance and adhesion of the plated coating. Other ferrous based parts may have some rust due to unprotected storage. This "soil" must be removed by the metal finisher to avoid contamination of his processing solutions and to obtain adhesion of the coating to the plated part. Pre-cleaning refers to the processing a metal finisher may perform on parts before they are routed through the plating line. Pre-cleaning is typically accomplished in one or a combination of the following procedures:



A. Vapor Degreasing

A vapor degreaser typically consists of a stainless steel tank with a compartment at the bottom for boiling one of several solvents, such as trichloroethylene, perchloroethylene, methylene chloride, Freon, or 111 Trichloroethane. The boiling solvent creates a vapor zone within the walls of the tank. The vapors are condensed using cooling coils near the top of the tank. There are several variations of how to vapor degrease but the basic principle involves hanging the greasy parts in the vapor zone on stainless steel hooks or wire. Larger degreasers for small parts are automated and the parts enter in steel trays and are automatically routed through the equipment. Since the parts entering

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the degreaser are cooler than the vapor, the solvent condenses on the parts and flushes off the oil/grease. The parts emerge from the degreaser in a relatively dry state, although some solvent may be trapped in pockets or drilled holes. The solvent/oil mixture returns to the boiling chamber, where the solvent is re-boiled, while the oil/grease remains in the mix. Eventually, the oil/solvent mix must be removed, replaced, and disposed of.

Pickling/Descaling/Blasting

Heavy Scale/Rust-Pickling or Blasting

Pickling: Strong Acid (eg. Hydrochloric)
Descaling: Alkaline-Permanganate
Strong Acid

Blasting: Last Resort (Expensive)
Normal in Hard Chromium
Plating Operations

B. Pickling/Descaling/Blasting

Heavily rusted or scaled parts need to be processed through an operation that removes the heavy oxide from the surface of the part. There are a number of ways to accomplish this, including blasting with nutshells, sand, or other "grit", pickling in strong solutions of acids, or descaling in an alkaline descaling solution consisting of concentrated sodium hydroxide and potassium permanganate at high temperature. Pickling and descaling is normally performed "off-line", because they are time consuming operations. The operation generates spent pickle liquor/descaling solution or contaminated blasting media.

II Metal Finishing Process Overview
Cu+1
Cu0
Typical Cleaning Tank With Continuous Oil Removal
Spray On Return Keeps Floating Oil Off Parts
Recirculating Pump
Screen For Solids Removal
Skimming Trough
Side Tank To Cool Cleaner and Float Off Oil
Tap To Remove Free Oil

C. Soak Cleaning

A soak cleaning tank typically consists of a steel tank containing a cleaning solution consisting of strong alkalies, various other ingredients and detergents mixed with water

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at temperatures from 160-200 deg. F. The parts to be cleaned are racked or in plating barrels and are immersed in the cleaning solution and the oil and grease is either emulsified or converted to soaps through saponification. The parts emerge from the soak cleaner coated with hot cleaner that then is either rinsed off before further processing, or is dragged into the next process. Soak cleaners are normally incorporated into the plating process line and are usually the first tank the parts go into, so they may also be considered part of the Pre-Plate operations described below. Soak Cleaners have a finite life due to the consumption of ingredients and accumulation of floating and dispersed oils, greases and organic compounds. Many soak cleaners employ skimming devices to remove floating oil.grease, in an effort at extending the life of the cleaner. Modern ultrafiltration systems have also been developed to remove contaminants so that the cleaner lasts much longer.

PRE-PLATE OPERATIONS
* Needed due to reduction of cyanide use
* Removes last traces of soils and oxides

CLEANING - Electrocleaning follows degreasing or soak cleaning
Electrocleaner & DC current decomposes H_20 into H & 0
Direct (parts neg. charged) or Reverse (parts pos. charged)
Followed by rinse water

ACID DIP/PICKLES - Neutralize alkali and remove surface oxides
Followed by rinse water

SPECIAL DIPS - Prevent reformation of oxides when exposed to air (aluminum)

STRIKES - Solution that provides thin protective coating of metal that will not react with the plating solutions

2. PRE-PLATE OPERATIONS

Pre-cleaning removes the bulk of the oils, greases, rust, scale or other soils present on the parts. In "the old days", when most plating solutions contained large concentrations of cyanide, pre-cleaning often was all that was required prior to plating. Modern metal finishing operations have replaced many cyanide solutions with non-cyanide chemistries and have reduced cyanide concentrations in those processes where cyanide remains, so pre-cleaning is not enough to prepare the parts for plating. The pre-plate operations must be tailored to the type of metal processed and the conditions of the surface of the parts. The object of the pre-plate process is to remove the last traces of surface soils and to remove all oxides from the surface. The following pre-plate processing steps are typical: (vapor degrease is not included, but may be required). Note that wherever a new processing step is indicated, additional waste is most often generated:

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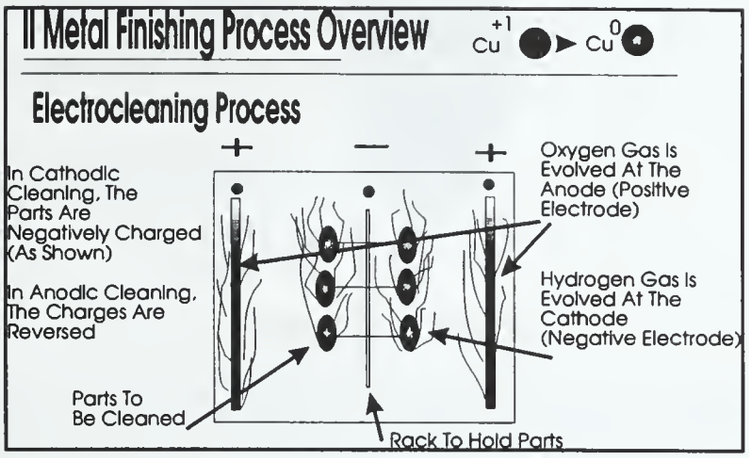
II Metal Finishing Process Overview
Cu +1
Cu 0
Electrocleaning Process
+
—
+
In Cathodic Cleaning, The Parts Are Negatively Charged (As Shown)
In Anodic Cleaning, The Charges Are Reversed
Oxygen Gas Is Evolved At The Anode (Positive Electrode)
Hydrogen Gas Is Evolved At The Cathode (Negative Electrode)
Parts To Be Cleaned
Rack To Hold Parts

3. CLEANING

Degreased parts still require additional cleaning to remove traces of soils left behind by the pre-cleaning step. This is normally accomplished by an electrocleaning operation. Electrocleaning systems consist of a heated steel tank that contains a solution similar to the soak cleaner. The tank is equipped with a rectifier and steel or stainless steel electrodes hanging from bus bars on either side of the tank. Cleaning is normally the next process step after degreasing or soak cleaning. If the parts were vapor degreased, they are either racked on plating racks or scooped/shoveled into plating barrels for cleaning. The racks or barrels are immersed into the electrocleaner and a DC current is passed through the parts. The current decomposes the water into two gases, oxygen and hydrogen. It is these gases, which are discharged in finely divided bubbles that do the cleaning. If the parts to be cleaned are negatively charged during this process, then hydrogen bubbles (commonly referred to as "direct" cleaning) are generated on the parts. If the parts are positively charged (commonly referred to as "reverse" cleaning), then oxygen bubbles perform the cleaning task. In each case the opposing electrode generates the other gas. The choice of direct vs reverse cleaning depends upon the type of metal to be cleaned, and its tendency to react with oxygen to form an oxide or the tendency for direct cleaning to deposit smuts. Both direct and reverse cleaning are sometimes performed either in sequence, with a periodic reverse rectifier, or through use of a rectifier and a reversing switch. Following electrocleaning, the parts are rinsed in water. Electrocleaner solutions have a finite life also, and typically need to be disposed of on a regular basis. Ultrafiltration and oil skimming on these cleaners can also be effective at increasing cleaner life.

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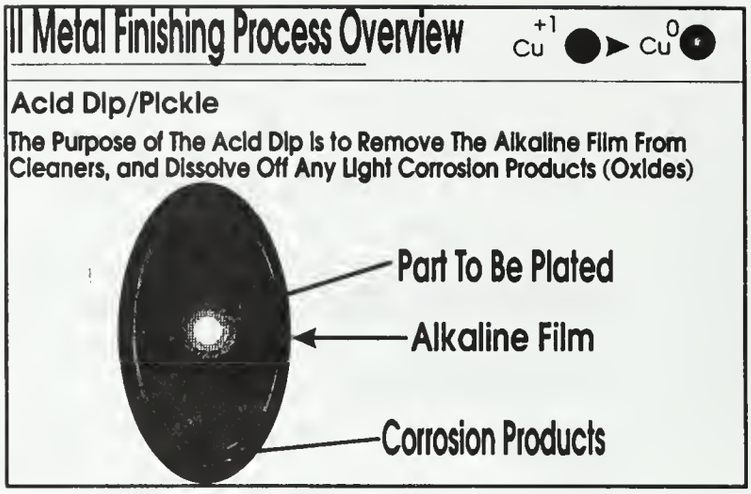
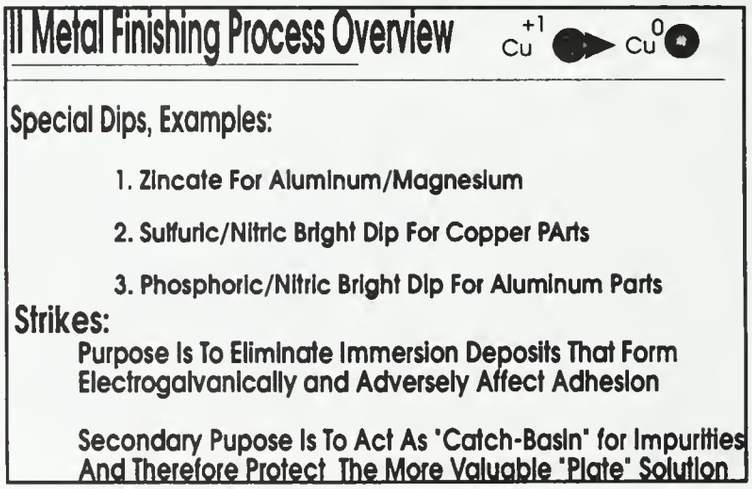

II Metal Finishing Process Overview
Cu+1
Cu0
Acid Dip/Pickle
The Purpose of The Acid Dip is to Remove The Alkaline Film From Cleaners, and Dissolve Off Any Light Corrosion Products (Oxides)
Part To Be Plated
Alkaline Film
Corrosion Products

4. ACID DIP/PICKLES

Parts that have been electrocleaned still have a thin alkaline film remaining, even after prolonged rinsing. This film must be removed for adequate adhesion to take place in the plating tank. Additionally, the parts may have a thin oxide film either formed during electrocleaning, or formed by exposure of the clean metal to air. This oxide also must be removed in order to obtain adequate adhesion of the plating. Lastly, some metals contain alloying elements that interfere with good adhesion. An example is lead which is added to brass to enhance the machining properties of the brass. The lead in the brass forms oxides that are not removed by the acids that are normally used before plating, such as sulfuric and hydrochloric. A special acid must be used to remove lead oxide from the surface of such brasses. The acid dip must therefore be of a chemistry that will neutralize alkali, and remove all surface oxides present on the part to be plated. After the acid dip, the parts are rinsed in water.

Acid dips and Pickles are consumed by neutralization of the acidity and the life of these dips is reduced by contamination with dissolved metals. The acids must periodically be disposed of through the waste treatment system. The life of an acid dip can sometimes be extended by careful control of dropped parts, use of acid sorption recovery methods, and control of acid strength (high strength dissolves too much base metal).


II Metal Finishing Process Overview
Cu+1
Cu0
Special Dips, Examples:
1. Zincate For Aluminum/Magnesium
2. Sulfuric/Nitric Bright Dip For Copper PArts
3. Phosphoric/Nitric Bright Dip For Aluminum Parts
Strikes:
Purpose Is To Eliminate Immersion Deposits That Form Electrogalvanically and Adversely Affect Adhesion
Secondary Pupose Is To Act As "Catch-Basin" for Impurities And Therefore Protect The More Valuable "Plate" Solution

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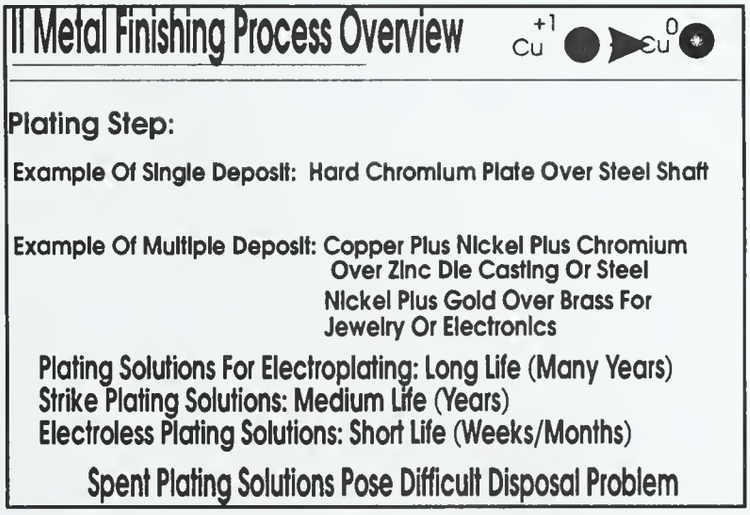
5. SPECIAL DIPS

Some parts are made of metals that re-form oxides as soon as the metal is exposed to air. An example is aluminum. Aluminum parts can be cleaned and acid dipped before plating and the plating will still not adhere, because the aluminum forms an oxide by reacting with the air as soon as the parts is removed from the acid, rinsed, and exposed to air. A special dip is therefore needed to prevent this from happening. The cleaned and acid dipped aluminum is dipped into a solution of sodium hydroxide and zinc oxide (often other ingredients are added) and water. In this solution, a controlled galvanic reaction occurs, where some of the aluminum dissolves and at the same time, some of the zinc coats the aluminum with a very thin film of zinc. The part that leaves this dip (called a zincate) is now coated with zinc, so there is no aluminum surface to react with the air. Special dips are subject to contamination and weakening through use. They therefore have a finite life and must be disposed of as concentrated wastes.

6. STRIKES

Some parts are made out of metals that react galvanically with certain plating solutions. An example is a zinc die casting or an aluminum part that has been dipped into a zincate. If we want to plate the zinc part, most plating solutions will chemically or galvanically attack the zinc. We therefore must use a specially designed solution called a "strike" to apply a thin protective coating of metal that will not react with the plating solutions. For zinc, or zincated aluminum, such a strike typically is a cyanide copper strike solution (described later). Some metal can not be adherently plated without first applying a thin strike deposit from a specialized strike plating solution. An example is stainless steel, which has a rapidly forming oxide that must be simultaneously removed in a special nickel strike solution, while a thin film of nickel is deposited over the stainless steel to prevent the reformation of the oxide. The nickel strike solution is purposely formulated to yield a thin deposit, while generating a large amount of hydrogen that reacts with the oxide on the stainless steel. Strike plating solutions are typically formulated to have a long life, lasting many years, unless contamination occurs. These solutions are very difficult to purify, when contaminated above tolerable concentrations, and at that time become wastes that require disposal.


II Metal Finishing Process Overview
Cu+1
Cu0
Plating Step:
Example Of Single Deposit: Hard Chromium Plate Over Steel Shaft
Example Of Multiple Deposit: Copper Plus Nickel Plus Chromium Over Zinc Die Casting Or Steel
Nickel Plus Gold Over Brass For Jewelry Or Electronics
Plating Solutions For Electroplating: Long Life (Many Years)
Strike Plating Solutions: Medium Life (Years)
Electroless Plating Solutions: Short Life (Weeks/Months)
Spent Plating Solutions Pose Difficult Disposal Problem

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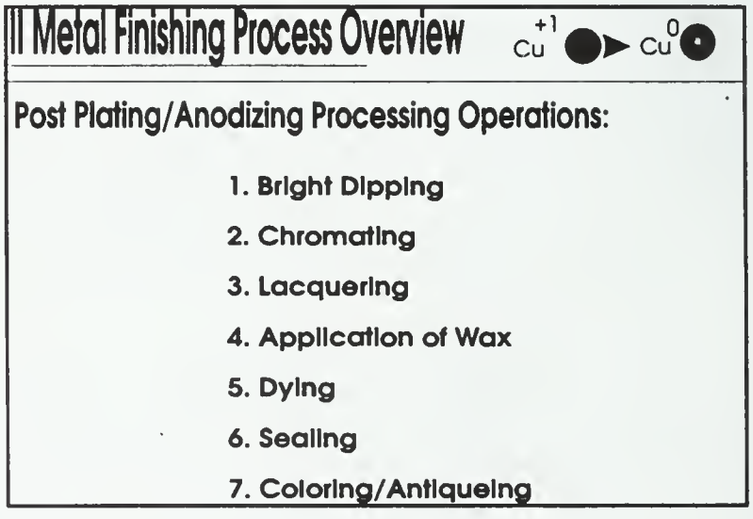
7. PLATE

The plating step may be a single plate or a series of different deposits. If a series of deposits is to be applied, there usually is a rinse and an acid dip between the different plating steps. For example, a zinc die casting may be plated with a cyanide copper strike, followed by a cyanide copper plate, followed by a semi-bright nickel plate followed by a bright nickel plate followed by a thin deposit of chromium. No rinsing or acid dipping may be required between the cyanide copper strike and the cyanide copper plate, or the semi bright nickel and the bright nickel, because the chemistries of the sequential baths are similar. However, there will be a rinse and an acid dip between the cyanide copper plate and the semi-bright nickel because one solution is alkaline and the other is acidic. There will be a rinse between the bright nickel plate and the chromium plate to prevent contamination of the chromium plating solution with nickel. There may or may not be an acid dip, since both solutions are acidic. After all plating has been performed the parts are rinsed and dried before packaging them for shipment.

Most plating solutions are formulated to provide a long life (many years), as long as impurities are periodically removed (creating waste), and reasonable care is taken by the plater to not contaminate the solution with excessive concentrations of contaminants. Certain plating solutions (especially "non-cyanide" versions of cyanide formulations) are very sensitive to metallic contamination and may have reduced life.

All electroless plating solutions have a relatively short life span, when compared to electroplating solutions (months vs years). All spent plating solutions are very concentrated and pose waste treatment difficulties/hazards. They typically are sent off site for disposal or heavily diluted prior to in-house treatment..



8. POST PLATING PROCESSING

Some plated parts are further processed to yield additional corrosion protection or to change the color of the deposit. Examples of such further treatment include the application of waxes or lacquers (see "polyseal" in example 4) to enhance the tarnish resistance and chromate conversion coatings following zinc, cadmium or other plated deposits to yield chromate films that range in color from transparent to olive drab green. Brass plating is often treated with various chemical solutions to turn the brass to differ colors ranging from green to black (even red is possible). All such subsequent treatments

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typically involve dipping the rack or plating barrel in one or more chemical solutions in various tanks and then rinsing off those solutions. Such solutions often contain ingredients such as nitric acid, sodium dichromate, selenium, arsenic, antimony, or other hazardous ingredients. The processing tanks and associated rinses may be incorporated into the plating line, or the operation may be carried out "off-line".

End Chapter 2

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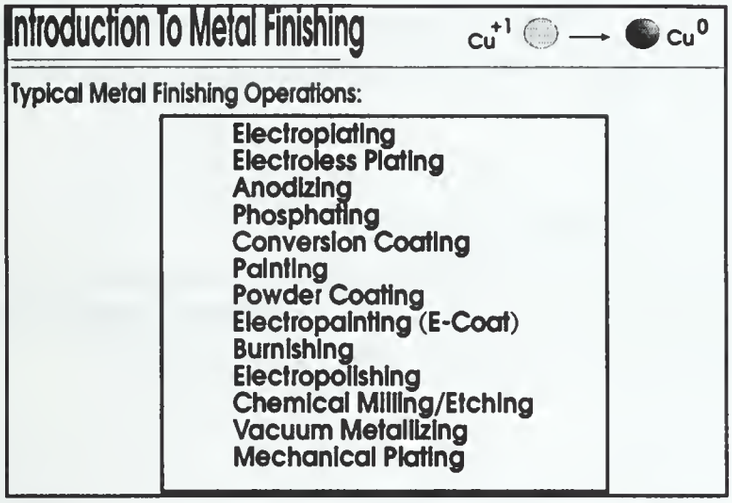
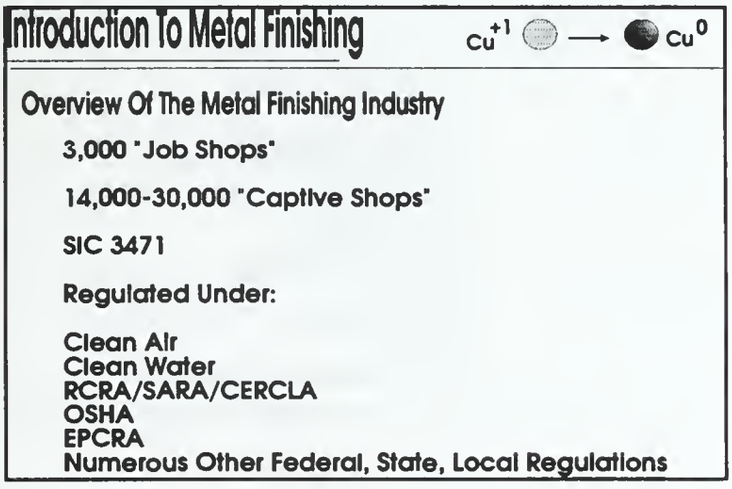
Part III,

Metal Finishing Process Details

The metal finishing industry provides a vital public service; that of protecting all kinds of metals (and non metals) from corrosion, excessive wear, or electrical malfunction.

Metal finishing is more than electroplating. It is the creation of a coating/coatings on a metal or non metal substrate by chemical, electrochemical, or physical means. The following processes are typical metal finishing operations:





In the United States, there are approximately 3,000 small companies that perform "job shop" electroplating. They are considered a service industry, in that they take parts manufactured by others, apply a metal finishing process or processes to those parts, and then return them to their client. In addition to job shop metal finishers, there also are "Captive" metal finishing facilities. Captive facilities are typically owned by large corporations and perform metal finishing processes as part of the manufacture or overhaul of a product manufactured by the large corporation. There is no accurate estimate of how many captive metal finishing facilities exist in the United States today. Estimates from 14,000 to 30,000 have been given in the past.

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All metal finishing facilities are regulated on a national and local level under numerous agencies enforcing various regulations, including the Clean Water Act, RCRA (Resource Conservation and Recovery Act), SARA (Superfund Amendments and Re-authorization Act) CERCLA (Comprehensive Environmental Response, Compensation and Liability Act), EPCRA (Emergency Planning and Community Right To Know Act), the Clean Air Act, and OSHA (Occupational Safety and Health Act).

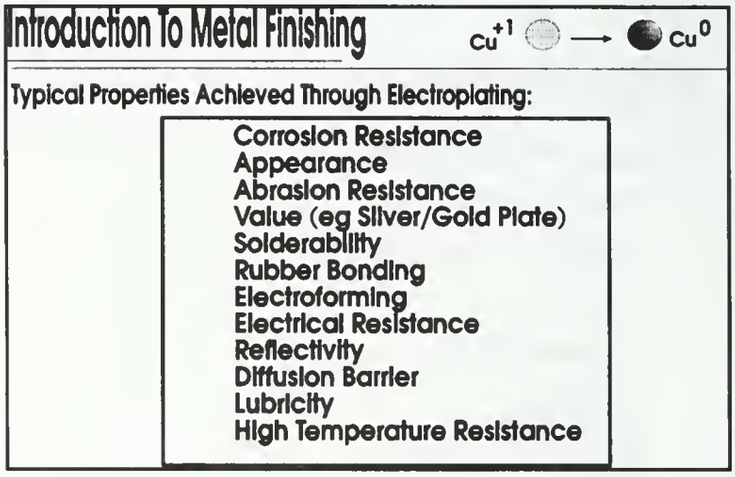
In order to comply with provisions of the Clean Water Act, most metal finishing companies operate pretreatment systems to remove pollutants before their process water is discharged either to a stream (under NPDES permit) or to a sewer system (under discharge authorization from the POTW). These pretreatment systems typically generate a solid waste that is regulated under RCRA.

Most metal finishing facilities utilize toxic/hazardous chemicals that are regulated under OSHA, CERCLA, EPCRA, and SARA. These include cyanides, various acids, strong alkalies, powerful oxidizers, and numerous flammable and non flammable organics.

ELECTROPLATING

CHOOSING THE RIGHT PLATED COATING

The choice of what metal(s) are to be plated on a part is usually made by the design engineer at the manufacturing site. Plated and chemically applied coatings are typically applied to enhance one of the following properties:



The designer will usually find that there is not much choice as to which combination of coatings is the best for his/her application. The plating combination that will provide the best compromise of cost vs the above benefits will usually be that specified for the part. The designer will then create a "specification" for the part that will detail the type of plating, the thickness range that each plated layer is to have, special properties (hardness, solderability etc.) that the plating is to have, and the subsequent coatings, if any, that are to be applied after plating. The following are typically plated metals and alloys and the possible reasons for specifying them:

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PLATED METAL	BENEFICIAL PROPERTY	COMMON USES
Zinc	Inexpensive Corrosion Protection	Hardware, Fasteners Automotive
Zinc-Alloy (Co, Ni, Sn, Fe)	Superior Corrosion Protection,	Cadmium Substitute
Cadmium	Corrosion Protection Lubricity Solderability Anti-fouling	Electronics, Hardware Fasteners, Aerospace Weapons Automotive
Copper	Ductile Underlayer Decorative Conductivity Diffusion Barrier	Electrical cable, Pennies, Die Castings Electronics, Carburizing Electroforming Automotive Plated Plastics Circuit Board Mfg.
Brass	Decorative Promotes Adhesion Of Rubber To Steel	Furniture, Hardware Vulcanizing, Consumer Items
Bronze	Decorative Lubricity	Consumer Goods, Bearings

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PLATED METAL	BENEFICIAL PROPERTY	COMMON USES
Nickel	Decorative	Consumer Goods
	Wear Resistant	Electroforming
	Anti-Tarnishing	Electronics
	Corrosion Resistant	Tools
		Automotive
		Plated Plastics
		Circuit Board Mfg.
Chromium	Wear Resistant	Consumer Goods
	Anti-Tarnish	Aerospace
	Decorative	Automotive
		Heavy Equipment
Gold	Low Electrical Resistance	Electronics
	Anti-Tarnish	Aerospace
	Decorative	Automotive
		Jewelry
		Printed Wiring Boards
Silver	Electrical Conductivity	Electronics
	Appearance	Jewelry
	Solderability	Home Furnishings
Tin	Corrosion Resistance	Steel Stock For Cans etc.
	Solderability	Electronics
	Ductility	Circuit Board Mfg.
	No Toxicity	Food Utensils
Tin-Lead	Solderability	Electronics
	Corrosion Resistance	Circuit Board Mfg.

There are numerous other metals and alloys that can be plated to obtain specific benefits. These include precious metals other than gold and silver (Rhodium, Palladium, Ruthenium, Platinum), and some uncommon "common" metals and alloys such as Bismuth, Iron, Alballoy (Copper-Tin-Zinc). There are also "composite coatings" that can be plated. For example, one can plate a nickel-cobalt alloy containing finely dispersed particles of silicon carbide to enhance abrasion resistance. This, or a some other composite may one day be a substitute for chromium plating.

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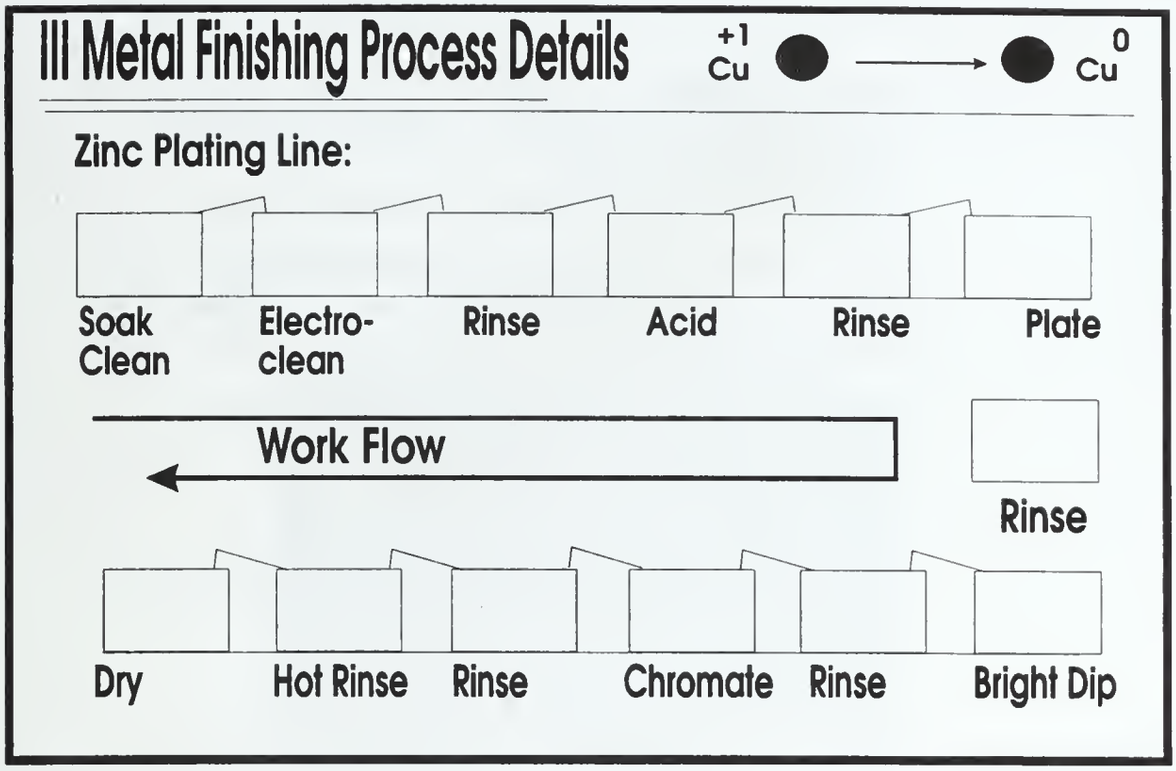

PLATING LINES/DEPARTMENT

Except for vapor degreasing, which normally is performed off-line, plating operations are normally incorporated into a sequence of tanks, called a "line".

A plating line may be designed to produce a single coating or a number of coatings. While not always the case, the process line contains tanks lined up in sequential order. Automated lines may or may not contain tanks in sequential order.

A zinc plating line may therefore consist of 13 tanks, each containing a chemical processing solution or rinse water; soak clean, electroclean, rinse, acid, rinse, zinc plate, rinse, bright dip, rinse chromate, rinse hot water rinse, dry. If the line is for barrel plating, each tank may have one or more "stations", that is places to put a barrel. A six station zinc plating tank can plate six barrel loads of parts at one time. To economize, some shops may have one cleaning line that services several plating lines. There also are tanks for rack stripping, stripping rejects, purifying contaminated solutions or holding solutions that are only sporadically used. The entire lineup of tanks and lines creates a "layout" of the shop, with parts entering the plating department from one direction, travelling through the process lines, and leaving the plating department.

THE ELECTROPLATING PROCESS

Electroplating is a process for coating a metallic or non metallic substrate, with a metallic coating through the use of a combination of electricity and a chemical solution that includes the ions of the metal in the coating. To conduct the process, we first need to purchase some hardware.

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Simple electroplating hardware consists of:

Simple Electroplating Hardware

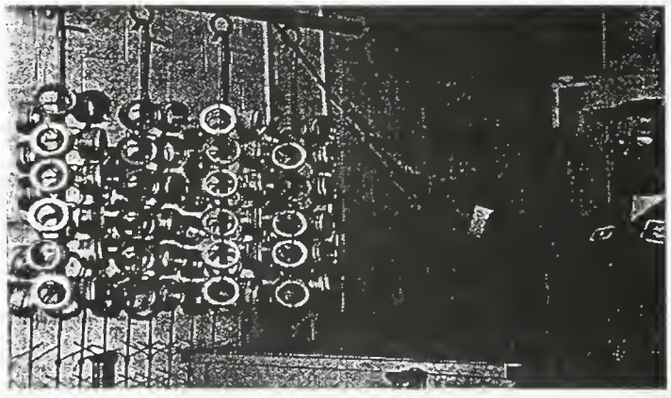
Rack or Barrel To Hold parts and Make electrical connection
Tank to contain plating solution and accessories
A power supply such as a DC generator, battery, or rectifier
Filtration equipment (optional in some plating processes)
Agitation Equipment (optional in some plating processes)
Ventilation Equipment (may be optional)
Plating Solution
Other processing tanks for cleaning, rinsing, acid pickling and waste treatment

METHODS OF PLATING

Plating can be performed using three main methods of part handling, each requiring different hardware:

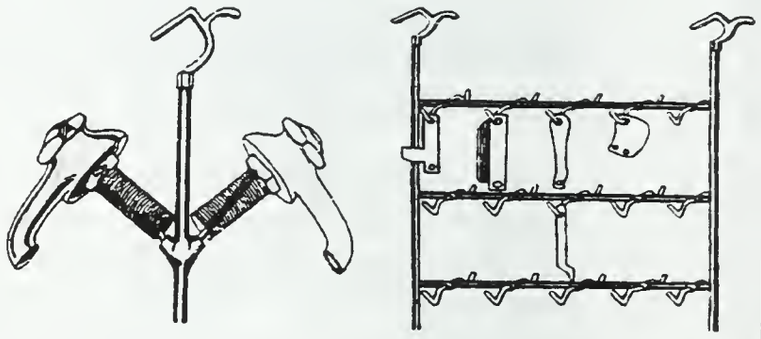
III Metal Finishing Process Details Cu^{+1} → Cu^{0}

Rack Plating:



III Metal Finishing Process Details Cu^{+1} → Cu^{0}

Rack Plating:



Illustrations Courtesy of Belke Mfg. Chicago IL

A. RACK PLATING METHOD

Rack plating is sometimes referred to as still plating and is used whenever the parts are too large, delicate or complicated to be barrel plated. Rack plating is much more expensive than barrel plating because of the labor involved in putting the parts on the rack and taking them off after they are processed. Rack plating is performed by hanging the parts to be plated on "racks", which are typically plastic coated copper or aluminum rods, with stiff wires/hooks that hold the parts in place and make electrical contact, protruding at various intervals. Racks come in numerous designs and are most often constructed by outside vendors and sold to the metal finisher. Some small parts are "racked" simply by twisting a thin copper wire around them. The wire, with perhaps 20-50 pieces hanging on it is then handled as a "rack". During plating, the part of the rack that makes electrical contact with the part being plated is also plated, so after several cycles, these contacts have a lot of metal buildup.The

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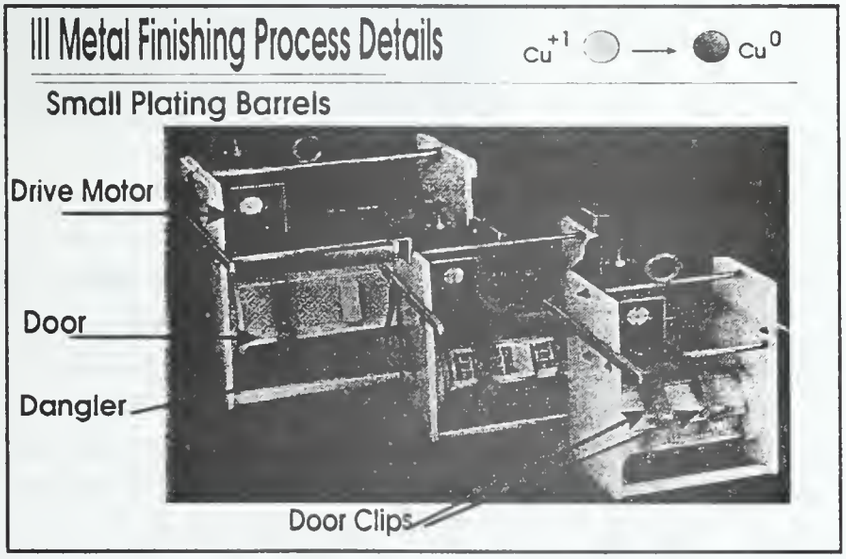
racks are then sent through a stripping solution that removes the excess metal, or the plater physically removes the excess metal using pliers or a hammer. Chemical rack strippers are usually strong solutions of cyanide or acid and can be difficult to waste treat. Non-cyanide and regenerative strippers are available for some processes, but are expensive to use or strip very slowly.

AUTOMATED RACK PLATING

Rack plating lines can be automated, using programmable hoists and process controllers. Automated lines yield better product uniformity, provide higher production rates, and generate less waste due to the ability to program and reproduce adequate processing, draining, and rinsing times for the racks.



B. BARREL PLATING METHOD

Barrel plating is the most efficient and least costly method. Plating barrels of varied designs are purchased from manufacturers of such products. The basic barrel consists of a hexagonal cylinder, closed at both ends, with perforated walls made of polypropylene. A "door" that is held in place with plastic coated clips, is installed in one wall of the

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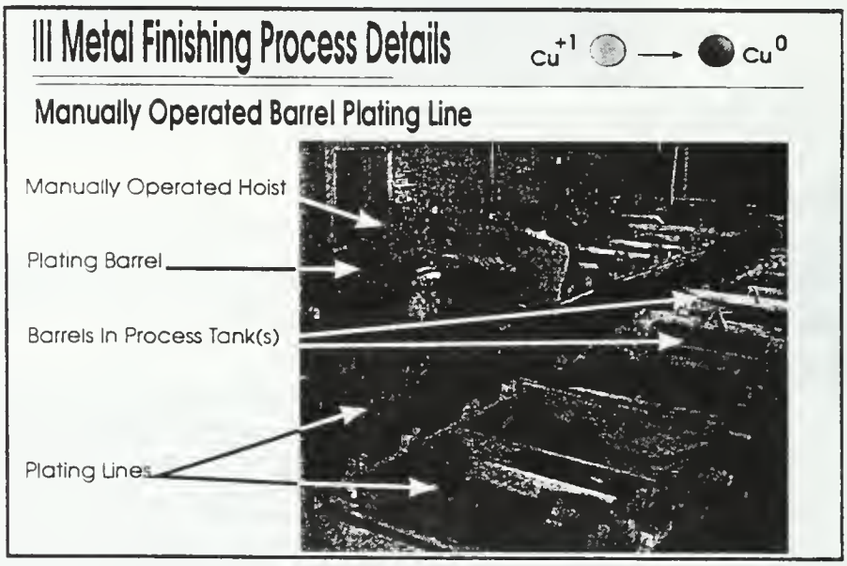
barrel to allow entry and exit of the load. Electrical contact between the saddle on the tank and the parts inside the barrel is made by a copper or bronze rod attached to the barrel that sits in the electrified saddle. The rod has a cable attached, and this cable is routed inside the plating barrel through the end of the barrel. Sometimes two cables are used, one entering each end of the barrel. The barrel has a hole in the center that allows for the cable to enter. The end of the cable, inside the barrel, has a stainless steel ball attached, called a "dangler". This dangler makes contact with the parts inside the barrel by gravity. There are other methods of making electrical contact inside the barrel, including rods and button contacts, but the dangler is the most commonly used method. Parts to be plated are scooped or shoveled into the barrel. The load is often weighed to make certain that the parts are uniformly plated. As a general rule, the barrel is never filled beyond 1/2 the total volume inside. As plating proceeds, a motor mounted either on the plating tank or on the barrel turns the barrel at 3-5 rpm, through either a drive belt or a set of gears mounted on the barrel. If the barrel was not rotated during plating, the top of the load would be plated and the bottom part would remain bare.



Barrel Plating can be performed on a manually operated plating line as illustrated above. The barrel is loaded and transferred from one process tank to the next by a worker using an electric hoist. The worker must take great care to keep the barrel in each process tank for only the required amount of time, so that each work load matches another in quality. Workers must also make certain that each barrel is drained as completely as possible after each process to reduce waste. The plating line should be designed to prevent drippage of process solution from draining to the plant floor. For economy, most barrel plating lines utilize lined and unlined steel tanks, which are prone to corrosion from the outside (as seen in the photo). If not properly maintained, this leads to tank perforation and costly process solution loss.

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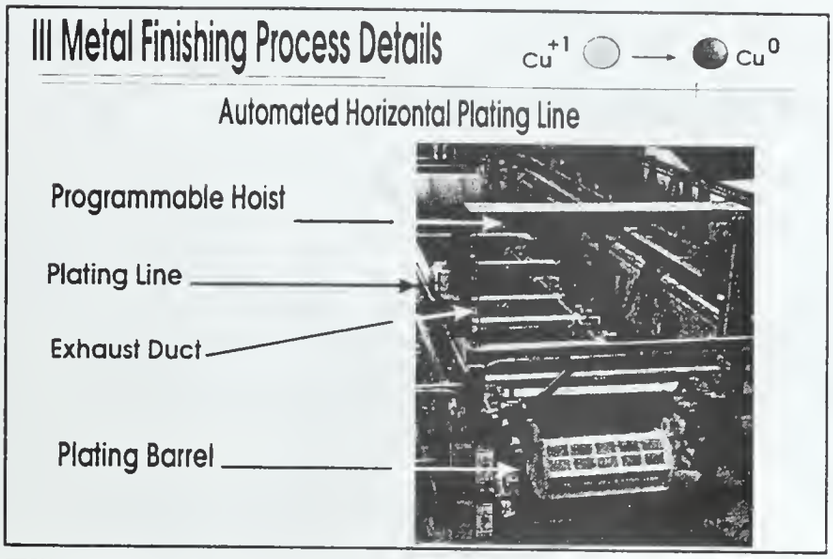

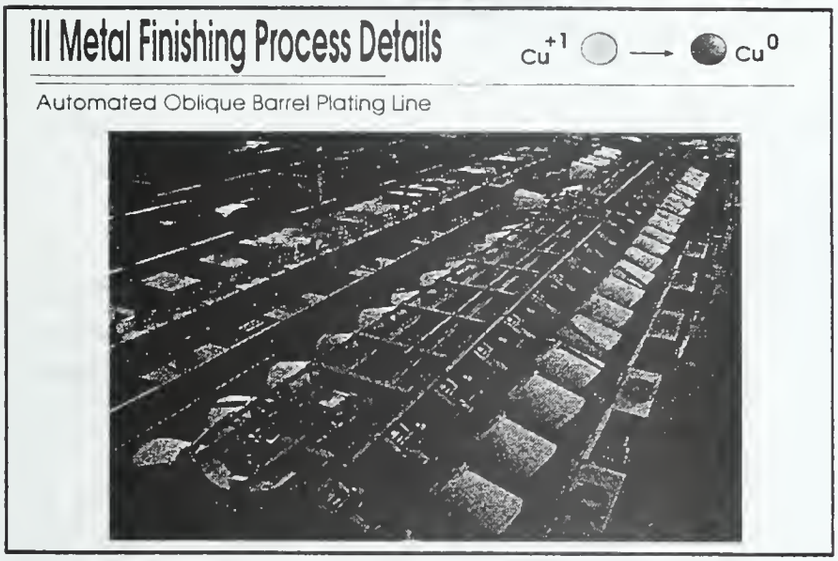

AUTOMATED BARREL PLATING

The barrel plating operation can be automated by the addition of a programmable hoist to move the barrels and keep track of process times. The newest facilities also incorporate process controllers and even analyzers to automate the process operating conditions and solution chemistries. The programmable hoist line utilizes horizontally oriented barrels that are difficult to automate for loading/unloading. The oblique barrel plating machine shown above, allows for automated loading/unloading because the top of the plating barrel is open. The machine unloads by tilting the barrel upside-down. The oblique plating machine utilizes a return type conveyor to move the barrel from one station to the next. The barrel is lifted (shown in upper right corner) over the tank walls during transfer. In both types of plating machines, the plating thickness obtained is determined by the residence time in the plating tank. In the case of the oblique plater, residence is determined by the size of the plating tank, since the barrel must stay in the tank while the machine indexes (moves the barrel from one place to the next). For this reason, oblique plating machines have very large capacity plating tanks (some machines have 10,000 gallon plating tanks). This results in high operating costs. The barrel in a horizontal plating machine stays in place, reducing solution volume and operating costs. The oblique plater, however, has the advantage of higher productivity.

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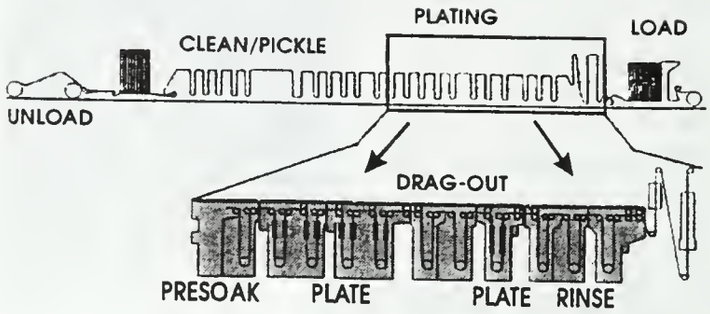
Continuous Strip Plating Schematic



C. CONTINUOUS PLATING METHODS

1. STRIP PLATING METHOD

This method of plating is highly efficient and competes effectively against all other methods, when the parts are small, uniform, simple geometry, and amenable to being stamped from a thin strip of metal, or when parts are small and must be "selectively" plated (plated only in specific areas). This method is used to electrogalvanize (zinc plate) steel strip that is used to stamp automobile bodies and to plate brass or copper strip for stamping electrical connectors for telecommunications. In this method of plating, the parts to be plated consist of long strips of metal that is rolled up into a coil. The coill is mounted on the equipment and the strip goes through a sequence of rollers directing it through various processing tanks, including the plating tank. The metal strip may partially dip into the plating tank, or be completely immersed. The strip may also travel through the plating line in vertical or horizontal orientation. Electrical contact is made either through metal brushes, rollers, or by a principle called "Bipolarity" (electromagnetically induced polarity), which does not actually contact the strip. The strip may travel at speeds ranging from 50 to 1000 or more feet per minute. The strip travels through the same process sequence as for regular plating (clean, rinse, acid, rinse etc.). At the other end of the continuous strip plating line, a second wheel takes up the processed strip. Continuous strip plating equipment is typically automated, except for process chemistry, and is very expensive to purchase, install and operate. The process must be very carefully monitored, or a large amount of waste (reject) material is produced in a very short period of time. This is especially important for continuous plating of precious metals such as gold, or silver.

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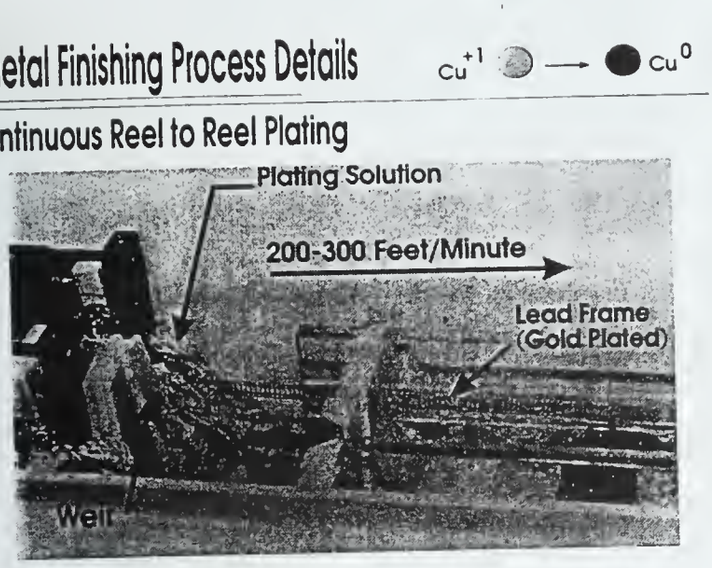
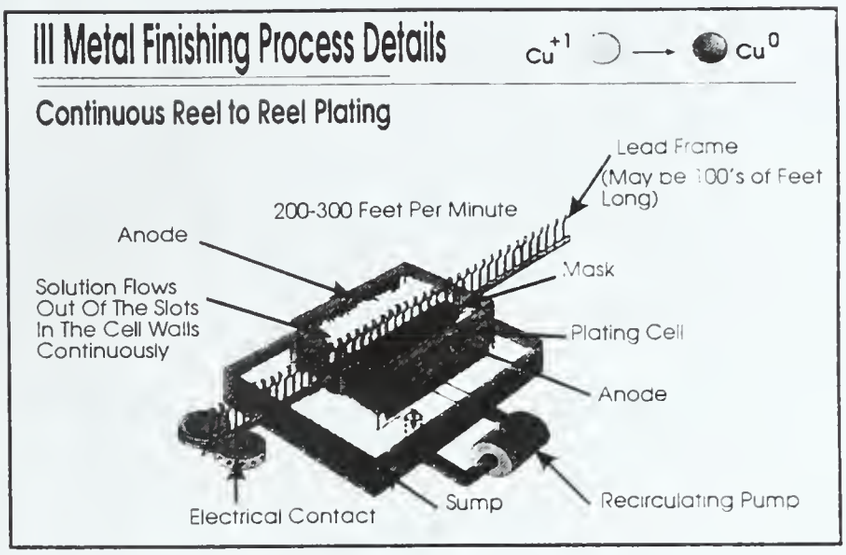
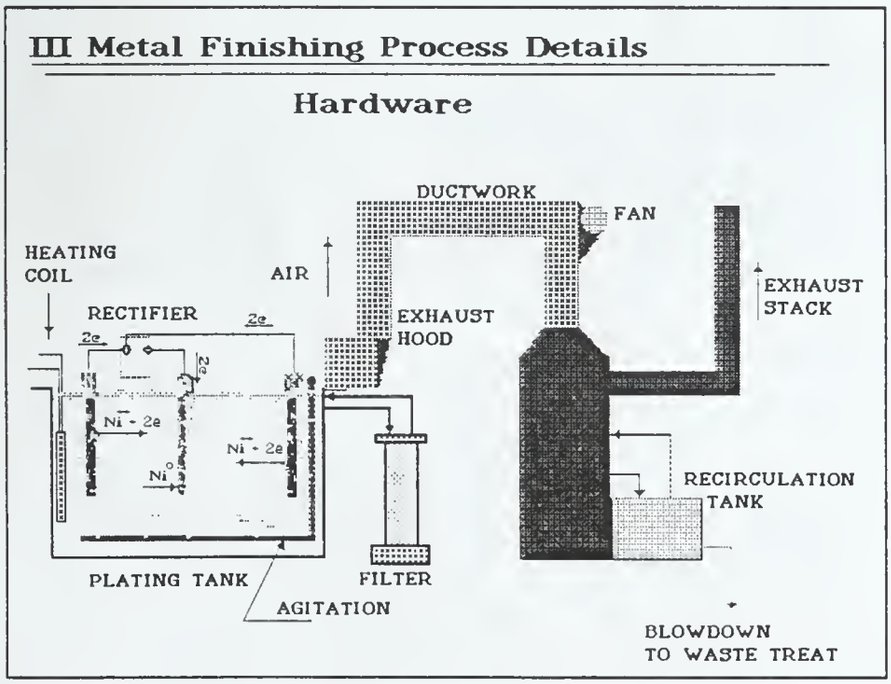




2. REEL TO REEL PLATING

This method of plating is similar in principle to strip plating, but this type of plating is usually on a much smaller scale. The tanks for reel to reel plating may only hold a gallon or a few gallons of plating solution. Below the plating cell is a sump tank that holds much more plating solution than the plating cell. The plating solution in the plating cell is continuously replenished via a recirculating pump. Reel to reel plating is commonly performed on electrical contacts for the telephone and computer industry. It is a far more efficient way to plate delicate parts than barrel plating.



HARDWARE

The hardware required to perform plating is typically purchased from a company that specializes in producing this equipment, although some platers produce their own hardware. Let's take a closer look at the hardware used for plating:

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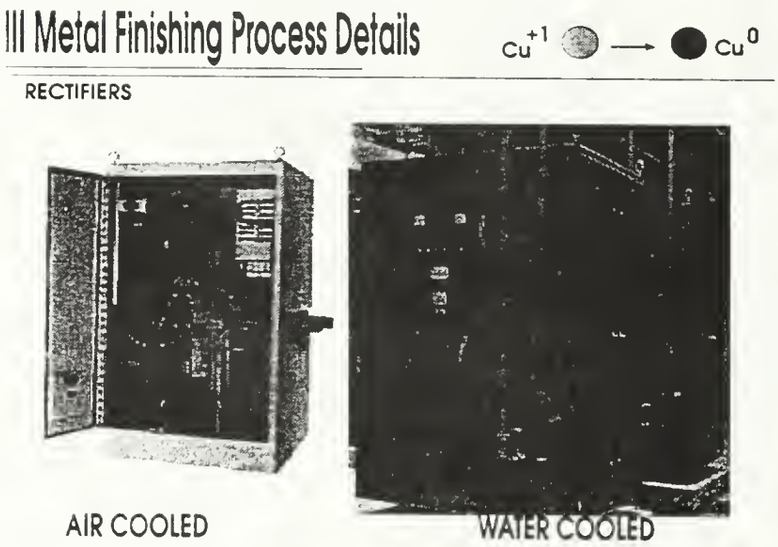
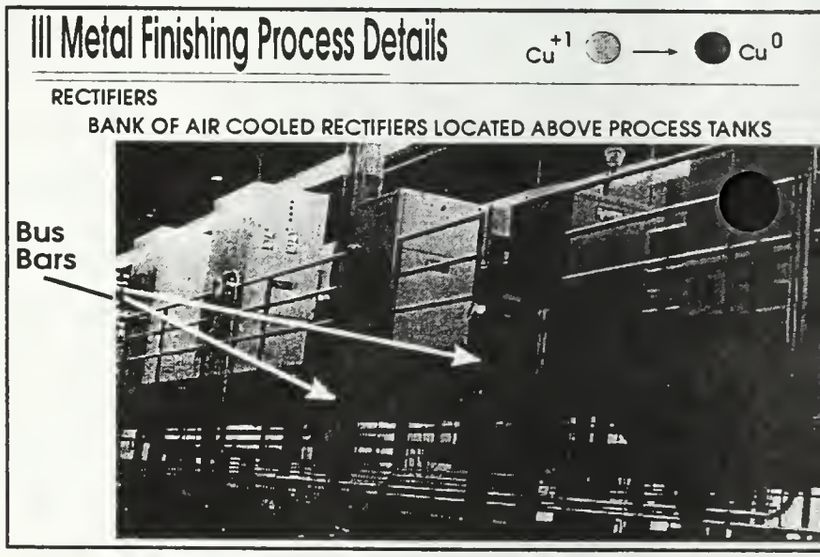
1. TANK

The plating tank must resist chemical attack from the plating solution. Tanks containing cyanide plating solutions are often made of bare steel. Tanks for other plating solutions are typically made of steel with PVC lining, polypropylene, polyvinyl chloride, or polyethylene. Plating tanks should not have any wall perforations below the liquid line, prevent accidental discharge of contents. Whenever possible, a tank should be made from non corrodible materials such as polypropylene, polyethylene, Kynar, PVC,or fiberglass. If the tank must be metal, it should be made from stainless steel or lined stainless steel.

A "rack" plating tank typically has three copper bus bars mounted on top of the tank. One bus is in the center and is used to hang the parts in the plating solution. The other two bus bars are located near the walls of the tank, and are used to hang anodes or "baskets" for anodes.

A barrel plating tank has the same anode bus, but there is no center bus. Instead, the tank typically has four "saddles" made of copper or bronze, mounter to the lips of the tank, so that the barrel contact rods can sit firmly in the saddles. At least one of the four saddles has a cable, or copper bus attached to it for contact with the rectifier.




III Metal Finishing Process Details
Cu^{+1} → Cu^{0}
RECTIFIERS
BANK OF AIR COOLED RECTIFIERS LOCATED ABOVE PROCESS TANKS
Bus Bars

2. RECTIFIER

The rectifier for plating converts the AC current to DC. The rectifier is typically installed near the plating tank, but may be located in a separate room (in which case a remote control is installed near the tank). In either case, cable or bus bar is used to connect from the positive terminal of the rectifier to the anode bus bar on the tank. The negative terminal of the rectifier is connected by cables or copper bus to the saddle of barrel plating tanks or to the cathode bus of rack tanks. Rectifiers generate heat as a by-product. This heat must be removed by using either a fan (air cooled) or by circulating cooling water through the rectifier (water cooled). The water used to cool the rectifiers can be routed to other plating or processing operations such as rinsing.

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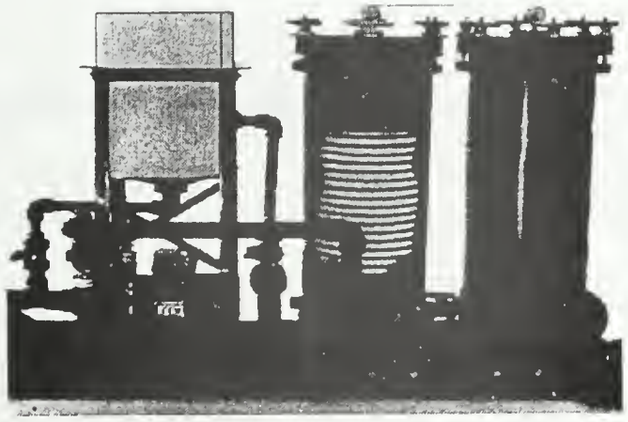
III Metal Finishing Process Details

Cu^{+1} ● ⟶ ● Cu^{0}

TYPICAL FILTRATION EQUIPMENT



3. FILTER

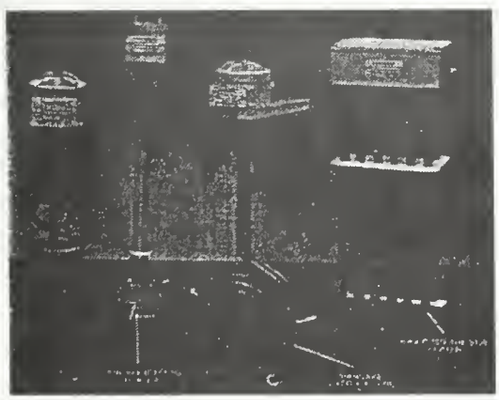
Some plating solutions require continuous filtration, while others do not. A general rule is that alkaline solutions can usually operate satisfactorily without a filter, while acidic solutions need filtration to avoid particulates suspended in the solution from being incorporated into the coating, yielding "roughness". Use of filters, even on tanks where it is not mandatory, almost always reduces rejects. While the filter shown in the slide is located outside the tank, it is recommended practice to locate the filter inside then tank whenever possible. If located outside, a containment dike or containment tank should be used, as there is spillage of process solution during servicing of the filter (replacement of filter elements or media).

Newer filters utilize re-usable media to avoid the need for disposing of spent filtration materials.

III Metal Finishing Process Details

Cu^{+1} ● ⟶ ● Cu^{0}

TYPICAL ELECTRIC HEATERS



4. HEATING EQUIPMENT

Many plating processes need to be operated at elevated temperatures, in order for the process to deliver the best performing deposit. Raising the temperature of the process can be performed by inserting a heating coil into the process solution and introducing steam into the coil. The most common alternate method of heating the process solution is to use electric immersion heaters.

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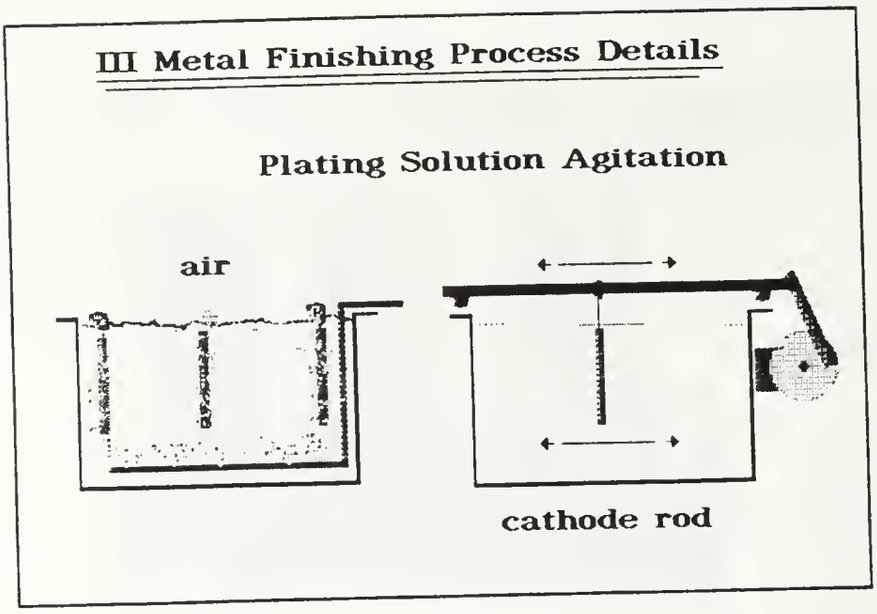
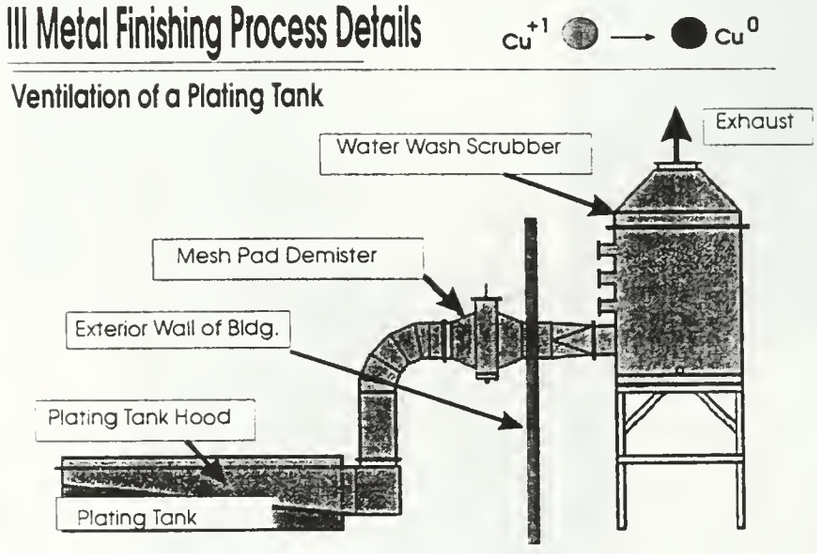


5. AGITATION

Most plating processes require some form of solution agitation to deliver the brightest, densest, most uniform deposit, and to plate at higher current densities without "burning". A common method of agitation is to move the cathode rod back and forth in the solution using a motor attached to the cathode rod. This is called cathode rod agitation. A second common method is to install an air sparger in the bottom of the plating tank and use low pressure air bubbles to perform the agitation. A less common technique is to use a prop mixer. Plating tanks for barrel plating are not agitated because the rotation of the barrel provides sufficient solution movement.



6. VENTILATION SYSTEM

Process solutions that emit mists or fumes during storage and use require a ventilation system to capture the offending emissions and emit them outside the process building (for worker safety and to protect equipment from excessive corrosion). If the emissions contain air pollutants that must be controlled, the ventilation system will include a scrubber or demisting system. Scrubbers and demisting systems use water sprays, and therefore generate a contaminated wastewater that must either be recycled back to the process or waste treated. Regulations under the Clean Air Act on solvent and (pending)

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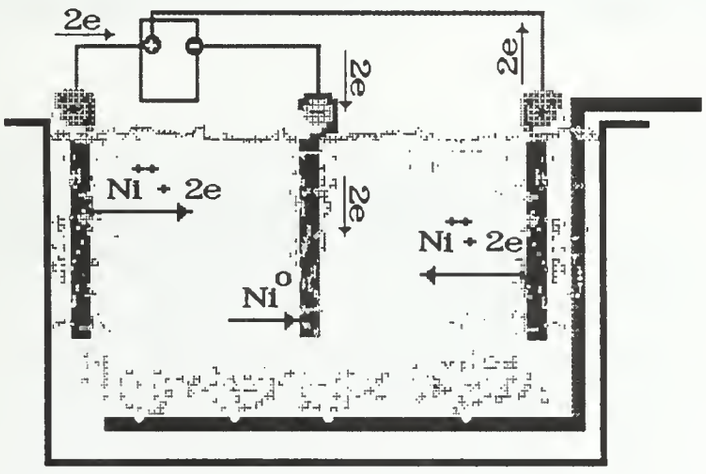
chromium emissions cause the metal finishing industry to install more equipment for removal of pollutants from ventilation systems.
Plating and processing solutions that typically require ventilation systems and scrubbing equipment are:

Processes Requiring Ventilation/Scrubbing:

	Ventilation	Scrubbing
Chromium Plating (Cr^{+6})	X	X
Nickel Plating (Air Agitation)	X	
Woods Nickel	X	X
Hydrochloric Acid	X	X
Nitric Acid	X	X
Hot Cleaners	X	
Electrocleaners	X	X
Electroless Nickel	X	

III Metal Finishing Process Details

Basic Plating Mechanism



THE PLATING SOLUTION

The plating solution normally contains water and a number of ingredients that determine if the coating produced is dense, bright, hard, a certain color, or a number of other desirable properties that can be obtained through chemistry. It also contains an ingredient that forms ions of the metal to be plated when added to water. For example, one ingredient in a watts nickel plating solution is nickel sulfate. When nickel sulfate is added to water, it dissolves and forms nickel ions and sulfate ions, just like when you add salt to water, it dissolves form sodium and chloride ions. The dissolved nickel ions can be converted to nickel metal by passing a direct current through the plating solution using the rectifier (which converts AC current to DC), the anode is the electrode with positive polarity, and the part we want to electroplate is the electrode with negative polarity. The conversion of the nickel ions to nickel metal will occur on the surface of the negative

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electrode, where excess electrons (which make the electrode negatively charged) "reduce" the nickel from ions to metal. While nickel ions are converted to metal at the cathode (negative electrode), at the anode, nickel metal is converted from the metal back to the ions. Ideally, for each nickel atom plated out at the cathode, we will form a new ion at the anode to replace the one plated out. This is the case in most plating solutions, but there are some solutions where the anode is not converted to metal ions. In cyanide based solutions, metal is plated from metal ions complexed with cyanide. In cyanide zinc plating solution, zinc is plated from two complexes, the metal-cyanide complex, and a complex between the zinc and hydroxide (called a zincate complex). Tin is plated from an alkaline stannate complex in the alkaline tin plating solution.

TYPICAL PLATING SOLUTION CHEMISTRIES

We will now briefly discuss the ingredients of the most commonly used plating solutions:

1. ZINC

Zinc is the most commonly plated metal, normally applied over ferrous substrates for the purpose of enhancing the corrosion resistance. Zinc can be plated from a number of different chemistries, but the three most common ones are cyanide, alkaline non-cyanide, and acid
chloride.

A. Cyanide Zinc

The cyanide baths are favored when high thicknesses are required or when parts are to be plated and then deformed. Still widely used, cyanide zinc plating solutions contain:

CYANIDE ZINC SOLUTION (g/L)	
Zinc Cyanide	15-60
Sodium Cyanide	8-45
Sodium Hydroxide	74-100
Organic Brightener	As required
pH	14+
Operating Conditions:	
Temperature:	70-90 deg F
Anodes:	Zinc/Steel baskets
Current Density:	10-50 ASF
Agitation:	Cathode Rod/none
Filtration:	Not required
Color of Solution:	Straw colored
Sometimes has floating oily layer)	
Odor of Solution:	Aldehyde
Life	Many Years

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B. Alkaline Non-Cyanide

These baths can be substituted for cyanide baths without the need for major equipment modifications. The deposits tend to become brittle as the thickness increases and some parts that have been heat treated yield poor adhesion.

ALKALINE NON CYANIDE ZINC (g/L)	
Zinc Oxide	8-15
Sodium Hydroxide	75-110
Sodium Carbonate	0-22
Additives	As Required
pH	14+
Operating Conditions:	
Temperature:	70-90 deg F
Anodes:	Zinc/Steel baskets
Current Density:	5-45 ASF
Agitation:	Cathode rod/none
Filtration:	Not required
Color of Solution:	Pale Yellow
Odor of Solution:	Sharp odor
Life:	Many Years

C. Acid Chloride

These baths yield the brightest deposit. The process requires excellent cleaning and corrosion resistant equipment, however, and thick deposits tend to be brittle.

ACID CHLORIDE ZINC (g/L)	
Zinc Chloride	30-90
Potassium Chloride	100-150
Ammonium Chloride	22-38
Boric Acid	30-38
pH	4.5-6.0
Operating Conditions:	
Temperature:	70-115 deg F
Anodes:	Zinc/Titanium baskets
Current Density:	10-150
Agitation:	Air or cathode rod
Filtration:	Required
Color of Solution:	Pale yellow
Odor of Solution:	None, sharp with air agitation
Life:	Many Years

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2. CADMIUM

The vast majority of cadmium plating is performed from the cyanide based chemistry. The sulfate chemistry has made small in-roads, but often does not adequately cover heat treated steel parts that have high surface hardness. The sulfate process also requires a much higher degree of cleaning, or adhesion becomes marginal.

A. Cyanide Cadmium Baths

The cyanide based cadmium plating solution contains:

CYANIDE CADMIUM SOLUTION (g/L)	
Cadmium Oxide	22-38
Sodium Cyanide	75-150
Sodium Carbonate	22-100
Sodium Hydroxide	15-60
Brighteners/Additives	As Required
pH	14+
Operating Conditions:	
Temperature:	70-90
Anodes:	Cadmium/Steel Baskets
Current Density:	5-90
Agitation:	Cathode Rod/none
Filtration:	Not Required
Color of Solution:	Pale Yellow
Odor of Solution:	Aldehyde
Life:	Many Years

Acid sulfate based cadmium plating solution contains:

ACID CADMIUM SOLUTION (g/L)	
Cadmium Chloride	8-10
Ammonium Sulfate	75-115
Ammonium Chloride	10-22
Brighteners/Additives	As Required
pH	5-6
Operating Conditions:	
Temperature:	70-100 deg F
Anodes:	Cadmium, Titanium baskets
Current Density:	2-15 ASF
Agitation:	Cathode Rod
Filtration:	Required
Color of Solution:	Pale Yellow
Odor of Solution:	Sharp
Life	Many Years

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3. COPPER

Copper is plated from three popular chemistries, cyanide, acid sulfate, and pyrophosphate. Recently, patented alkaline non cyanide copper plating processes have been developed and marketed by at least three companies, but they are troublesome and expensive to operate.

A. Cyanide Copper Process

There are several cyanide copper plating processes, but they can be divided into two basic chemistries; a strike bath and a "plate" or high speed bath.
The ingredients/operating conditions are:

CYANIDE COPPER SOLUTIONS (g/L)

	Strike	Plate
Copper Cyanide	10-15	30-60
Sodium Cyanide	22-30	60-90
Sodium Carbonate	22-100	22-100
Sodium Hydroxide	0-10	15-30
Brightener/Additives	(none)	As Required
pH	10-10.5	12-14

Note: Potassium salts are most often used in high speed cyanide copper plating solutions, at approximately the same concentrations.

Operating Conditions:

Temperature:	140-160 deg F.
Anodes:	Oxygen Free High Conductivity (OFHC) Copper
Current Density:	10-100 ASF
Agitation:	Cathode Rod
Filtration:	Required
Color of Solution:	Pale Yellow
Odor of Solution:	Pungent
Life	Strike: Years Plate: Many Years

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B. Acid Sulfate Processes

There are two main acid sulfate chemistries used in electroplating copper. One is termed "conventional" and is often used as an underlayer for plated plastic, or in applications where a high degree of "leveling" (smoothing of scratches) is desired. The second process is called a high-throw bath, used mostly by printed wiring board manufacturers because of the ability to produce uniform thicknesses on the outside of a circuit board and on the inside of tiny holes drilled into the board.

ACID COPPER PLATING SOLUTIONS (g/L)

	Conventional	High Throw
Copper Sulfate	200-250	75-100
Sulfuric Acid	45-90	150-300
Chloride	40-80	40-80 ppm
Brighteners/Additives	yes	yes
pH	<1	<1

Operating Conditions:

Temperature: Room

Anodes: Copper containing 0.02-0.06 % phosphorus, bagged

Plating Current Density: 20-200

Agitation: Air

Filtration: Continuous

Color Of Solution: Deep Cobalt Blue

Odor Of Solution: No specific smell, inhaled mist may yield sharp odor/burning of nose

Life: Many Years

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PYROPHOSPHATE COPPER SOLUTIONS (g/L)	
Copper Pyrophosphate	75-90
Potassium Pyrophosphate	300-350
Potassium Nitrate	7.5-12
Ammonia	1-4
Additives	Variable
pH	8-9
Operating Conditions:	
Temperature:	125-135 deg F
Anodes:	Oxygen Free High Conductivity Copper Titanium Baskets
Plating Current Density:	10-90 ASF
Agitation:	Air
Filtration:	Yes
Color of Solution:	Iridescent blue/purple
Life	A Few Years

C. Pyrophosphate Copper Solutions

These plating solutions are almost exclusively used by printed circuit board manufacturers. Their major benefits include low copper concentration and the ability to deposit an even thickness over complex geometries, such as the top of a circuit board vs the inside of a drilled hole.

The majority of these solutions have been replaced with bright throw acid sulfate systems because the pyro baths are much more difficult chemistries to analyze and control. You may find the baths in some job shops as substitutes for cyanide copper strike baths on zinc die castings or for copper striking zincated aluminum.

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4. BRASS PLATING

Currently, there are no commercially viable processes for plating brass, and alloy of copper and zinc, other than from a cyanide based chemistry. Brass is applied mostly for decorative purposes, wherein it is subsequently stained to yield an "antique" or colored finish. Brass is also applied to enhance adhesion of rubber to steel. Brass readily tarnishes, so most often it is finished off with a coat of lacquer.

BRASS PLATING SOLUTION (g/L)

Copper Cyanide	30-60
Zinc Cyanide	8-15
Sodium Cyanide	15-30
Sodium Carbonate	22-100
pH	10-11.5

Operating Conditions:

Temperature:	125-135 deg F
Anodes:	Brass of same alloy composition as plated
Current Density:	5-15 ASF
Agitation:	Cathode Rod
Filtration:	Yes
Color of Solution:	Pale yellow
Odor of Solution:	No specific
Life	Many Years

BRONZE PLATING SOLUTION (g/L)

Copper Cyanide	35
Potassium Cyanide	80
Potassium Stannate	42
Potassium Hydroxide	12
Sodium Potassium Tartrate	45
pH	12+

Operating Conditions:

Temperature:	150-160 deg F
Anodes:	Copper/carburized Steel, graphite, or stainless steel
Current Density:	20-100 ASF
Agitation:	Cathode Rod
Filtration:	Yes
Color of Solution:	Pale yellow
Odor of Solution:	Pungent
Life	Many Years

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5. BRONZE

Bronze (80% Copper 20% Tin) can only be plated from a cyanide based chemistry. The plating equipment is identical to that for copper, or brass plating.

6. ZINC ALLOY

Alloys of zinc have been the major focus for a good substitute for cadmium plating. If an alloy of zinc contains a small amount of a more noble metal, such as nickel, tin, cobalt, or iron, the zinc retains its cathodic relationship with steel, but the alloying metal reduces the activity of the coating so that it corrodes sacrificially at a slower rate, thereby enhancing corrosion protection over plain zinc. There are numerous zinc alloy processes being touted as the best cadmium alternative, including zinc-nickel, zinc-cobalt, zinc-tin, and zinc-iron. Of these, zinc-nickel appears to be a favorite at this time while some zinc-cobalt installations have been made. The others are either too expensive or do not produce a pleasing enough appearance to be applicable for anything other than as a paint undercoat for automobile body panels. The equipment for plating zinc alloys is identical to that used for nickel plating (see below).

A. Zinc-Nickel

Zinc-Nickel alloys can be plated from both alkaline and acidic chemistries, with the alkaline process the most often favored.

Alkaline Zinc Nickel

ALKALINE ZINC-NICKEL SOLUTION (g/L)	
Zinc	8-15
Sodium Hydroxide	90-130
Nickel	1-1.5
Additives	As required
pH	14+
Operating Conditions:	
Temperature:	70-90 deg F
Anodes:	Zinc and Steel
Current Density:	10-45 ASF
Agitation:	Cathode Rod
Filtration:	Yes
Color of Solution:	Yellow
Odor of Solution:	No specific
Life	No Data (New Process)

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B. Zinc Cobalt

ACID ZINC COBALT SOLUTION (g/L)	
Zinc chloride	75-90
Potassium Chloride	200-250
Cobalt	2-3.5
Boric Acid	22-30
pH	5-6
Operating Conditions:	
Temperature:	65-95 deg F
Anodes: Zinc, bags	Current
Density:	1-40 ASF
Agitation:	Air
Filtration:	Yes
Color of Solution:	Pale with slight purple
Odor of Solution:	No specific
Life	No Data (New Process)

7. NICKEL

Nickel is most often plated from the "Watts" chemistry, although there are numerous other formulations, including a specialized "Woods Nickel Strike" that is used to obtain adhesion on stainless steels. The watts bath is used to obtain bright or semi-bright deposits for decorative applications. In decorative applications where deposit appearan and corrosion resistance are highly important, as on the exterior of an automobile, two or more layers of nickel from watts baths are applied. The most common such layered nickel plating is referred to as "duplex nickel" which consists of two layers of nickel. The first layer is called semi-bright nickel, containing no sulfur bearing brighteners and the second layer is a fully bright nickel deposit containing a controlled amount of sulfur bearing brightener.

The duplex nickel is normally topped off with a thin coating of chromium plating. The bright nickel layer corrodes in favor of the semi bright, protecting it galvanically and delaying the onset of corrosion of the base metal.

Another often used nickel plating formulation is the sulfamate based chemistry. It is used in electroforming or other applications where a nickel deposit containing no or low internal stress is desired.

Nickel is also used to plate "composite" deposits, where the plated nickel contains finely dispersed diamond dust or other abrasives such as silicon carbide. Such composite coatings are used to create long lasting cutting tools.

A. Watts Nickel

The watts nickel plating chemistry can contain a variety of additives to control pitting, yield "levelling", and produce brightness from a medium (semi-bright) to a full mirror bright deposit. Additives are normally patented products sold by suppliers along with t plating chemicals.

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WATTS NICKEL SOLUTION (g/L)	
Nickel Sulfate	225-350
Nickel Chloride	30-90
Boric Acid	30-45
Additives	As Required
pH	3-5
Operating Conditions:	
Temperature:	125-135 deg F
Anodes:	Nickel or Nickel containing 0.02 % Sulfur or others, Bagged
Current Density:	25-100 ASF
Agitation:	Cathode Rod or Air
Filtration:	Yes
Color of Solution:	Deep Green
Odor of Solution:	No specific
Life	Many Years

B. Wood's Nickel Strike

This bath is purposely designed to generate high volumes of hydrogen gas, while depositing only a thin layer of nickel, even at the highest current densities. The major use is to obtain adherent thin nickel deposits that can then be plated with other metals.

WOODS NICKEL STRIKE (g/L)	
Nickel Chloride	225
Hydrochloric Acid	100-200 ml/L
pH	<.1
Operating Conditions:	
Temperature:	70-90 deg F
Anodes:	Nickel
Current Density:	100-300 ASF
Agitation:	None
Filtration:	None
Color of Solution:	Dark Green
Odor of Solution:	Sharp Hydrochloric Fumes
Life	Years

C. Sulfamate Nickel

The sulfamate nickel chemistry is used mainly for electroforming purposes, although some electronic applications requiring a low stress nickel underplate for gold overplates also use this bath. The equipment for sulfamate plating is identical to that used for watts baths, with the exception that the sulfamate process will typically have a purification

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compartment attached to the tank, incorporated into the tank, or alongside the tank. The purification compartment is about 1/5 the size of the plating tank and the solution is

SULFAMATE NICKEL SOLUTION (g/L)	
Nickel Sulfamate	450-525
Magnesium Chloride	8-15
Boric Acid	45-55
Additives	As Recommended
pH	3-5
Operating Conditions:	
Temperature:	125-135 deg F
Anodes:	Sulfur Depolarized Nickel
Current Density:	20-140 ASF
Agitation:	Air
Filtration:	Yes
Color of Solution:	Deep Green
Odor of Solution:	No specific
Life	Many Years

recirculated through the compartment, using the filtration system. In the purification compartment, electrolytic nickel anodes and dummy electrodes plate out metallic contaminants and the polarization occurring at the anodes decomposes some of the sulfamate ions into stress reducing compounds.

D. Sulfamate Nickel Strike

An alternate strike solution can be used to activate stainless steel (vs the Woods Nickel Strike). This solution eliminates the hydrochloric acid, which causes a safety and ventilation hazard.

SULFAMATE NICKEL STRIKE	
Nickel Sulfamate	320g/L
Sulfamic Acid	150g/L
Operating Conditions:	
Temperature:	50°C
Anodes:	Electrolytic Nickel
Current Density:	50ASF
Agitation:	None
Filtration:	Yes
Color of Solution:	Deep Green
Odor of Solution:	No Specific
Life:	Years

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8. CHROMIUM

Chromium plating generally falls into two categories; decorative and "hard". Both categories can and are being plated from the same chemistries based on hexavalent chromium, while decorative chromium can also be plated from one of several trivalent chemistry. The terms decorative and hard are confusing and really mean "thin" and "thick". All chromium plates have a hardness in the same range (900-1100 vickers). Decorative chromium is a very thin layer of chromium applied over a substrate that has been bright nickel plated. The appearance of decorative chromium, to a large extent, is due to the appearance of the nickel. The chromium is so thin (3-20 millionths of an inch), that is essentially transparent. Decorative chromium plating equipment is identical to that of hard chromium. An exception is the trivalent decorative chromium, which typically has no exhaust system and requires continuous filtration.

"Hard" chromium should be called engineering chromium, because it is usually applied when a hard wear resistant metallic coating is required on a part that is subject to abrasive forces during service. A typical example is the chromium applied to hydraulic shafts for heavy equipment, on the piston rings of internal combustion engines, and on the shafts of landing gears of aircraft. A typical chromium plating tank is constructed of steel with a PVC lining. It is equipped with heating elements and an exhaust system to remove the chromic acid fumes from the workers' breathing zone.

CHROMIUM PLATING SOLUTIONS (HEXAVALENT)

Chromium Trioxide	225-260
Sulfate	2.25-2.6

Operating Conditions:

Temperature:	125-135 deg F

(for hard plating applications, temp. may be at 140 deg.F)

Anodes:	Lead
Current Density:	Decorative 100-150 ASF, Hard 150-250 ASF
Agitation:	None (Hard may use some air agitation)
Filtration:	No
Color of Solution:	Deep dark red-brown
Odor of Solution:	No specific
Life:	Many Years

Mixed Catalyst Solutions:

Chromium Trioxide	30-45 oz/gal
Sulfate	.15-.18 oz/gal
Fluoride	.13 oz/gal

Note: fluoride may be present as one or more of a variety of fluoride containing compounds.

Operating Conditions/Life: Same

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A. Hexavalent Chemistries

The hexavalent chromium plating chemistries fall into two categories, conventional, and mixed catalyst. The conventional is a simple chemistry that anyone can mix up and use. The mixed catalyst chemistries are patented processes that have a few advantages, including faster plating, less problems caused by current interruption, and fewer problems plating onto passive nickel deposits. They also tend to be more difficult to control and expensive to operate. In hard chromium applications, mixed catalyst baths also tend to etch steel in areas where plating is not intended, making masking more critical.

B. Trivalent Chemistries

Trivalent chemistries were developed in response to concerns about the detrimental effects of hexavalent chromium on the environment and workers' health. Hexavalent chromium is a powerful oxidizer that readily attacks human tissues and has been linked in some studies to lung cancer. Trivalent chromium has a much lower toxicity level, is not an oxidizer and has to date not been linked with cancer. Platers have been slow to accept trivalent chromium chemistries as substitutes for hexavalent chemistries because they tend to plate deposits that are noticeably darker or not consistently of the same color. Since trivalent baths are only used for decorative applications, this is a major drawback, but solution manufacturers have made great progress towards solving these problems. A major benefit from trivalent processes is that these baths contain very low concentrations of chromium (about 1/5th as much),and the chromium can be waste treated without a reduction step, so waste treatment and sludge disposal costs are reduced. Equipment generally consist of a rubber or plastic lined steel or plastic tank, an air agitation system, heating and cooling system, and a filtration system.

Trivalent Chromium Plating Solutions (g/L):

TC Additive	400
(Chromium Conc is	20
TC Stabilizer	8% vol
TC-SA	1.2 %vol
TC Regulator	1 ml/L
pH	3.2
Operating Conditions:	
Temperature:	70-90 deg F
Anodes:	Graphite (Harshaw)
	(Lead in membrane cell Enthone-OMI)
Current Density:	90-200 ASF
Agitation:	Air
Filtration:	Yes
Color of Solution:	Deep blue-Green
Odor of Solution:	No specific
Life:	Many Years

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9. GOLD

Gold can be plated from three major chemistries; alkaline cyanide, neutral, and acid. All three chemistries utilize gold from potassium gold cyanide salts. A proprietary gold plating process that does not utilize potassium gold cyanide is on the market, but is expensive to
operate and limited in alloying capability. Most gold plated is an alloy of gold and some other metal or combination of metals such as nickel, cobalt, copper and silver. Gold can be plated in any commercial "Karat" desired. The neutral and acid gold plating chemistries utilize chelating agents to perform the tasks normally performed by cyanide, control of metallic impurities and alloying elements. While these chelates could cause waste treatment problems, they rarely enter the wastewater treatment system in high concentrations, since most gold plating operations have meticulous recovery systems to use as little rinsewater as possible and recover the plating chemicals.

A. Alkaline Cyanide Chemistry

This bath is most often used to apply a thin film of gold over bright nickel in decorative applications such as jewelry. The plating tank is a typical layout with a plastic or lined steel tank, filtration, cathode rod agitation (optional), and heating elements.

CYANIDE GOLD PLATING SOLUTION (g/L)	
Potassium Gold Cyanide	1-4
Potassium Cyanide	1-12
Potassium Carbonate	22-200
Additives	As Required
pH	10
Operating Conditions:	
Temperature:	125-150 deg F
Anodes:	Gold or Stainless Steel or Platinized Titanium
Current Density:	1-35 ASF
Agitation:	Cathode Rod
Filtration:	Yes
Color of Solution:	Dark yellow
Odor of Solution:	No specific
Life:	Many Years

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B. Neutral Gold Plating Chemistry:
These solutions are favored for barrel plating applications of high purity gold.

NEUTRAL GOLD PLATING SOLUTION (g/L)	
Potassium Gold Cyanide	8-12
Monopotassium Phosphate	75-90
Potassium Citrate	60-75
pH	6-6.5

Operating Conditions:	
Temperature:	125-135 deg F
Anodes:	Platinized Titanium
Current Density:	1-3 ASF
Agitation:	Cathode Rod/Recirc Pump
Filtration:	Yes
Color of Solution:	Pale yellow/clear
Odor of Solution:	No specific
Life:	Many Years

C. Acid Gold Plating
Acid gold baths can produce a variety of gold deposits, including the hardest, most wear resistant. They are favored for plating of printed circuit board connectors and in the semi-conductor industry.

ACID GOLD PLATING SOLUTION (g/L)	
Potassium Gold Cyanide	4-8
Citric Acid	30-60
Ammonium Citrate	30-45
pH	3-5

Operating Conditions:	
Temperature:	90-140 deg F
Anodes:	Platinized Titanium or Platinized Niobium
Current Density:	1-5 ASF
Agitation:	Cathode Rod
Filtration:	Yes
Color of Solution:	Range from clear to purple
Odor of Solution:	No specific
Life:	Many Years

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SILVER PLATING SOLUTION (g/L)	
Silver Cyanide	8-30
Potassium Cyanide	15-30
Sodium Carbonate	22-100
Potassium Hydroxide	8-15
Potassium Nitrate	0-15
pH	12-14
Operating Conditions:	
Temperature:	70-90 deg F
Anodes:	Silver
Current Density:	1-40 ASF
Agitation:	Cathode Rod
Filtration:	Yes
Color of Solution:	Dark Brown/black
Odor of Solution:	Organic
Life:	Many Years

10. SILVER

While non cyanide silver plating chemistries based on sulfites or succinimides have been available for some time, most all silver plating is presently being performed in the cyanide chemistry. The non-cyanide baths are far more expensive to install and operate and can not tolerate contamination to the same degree as the cyanide process. The plating equipment is typically a lined steel or plastic tank equipped with a filter and cathode rod agitation. Silver can also be barrel plated.

11. TIN

Tin can be plated from more than four major chemistries; the alkaline stannate process, the fluoborate, the proprietary "halogen" and sulfonate processes, and the sulfuric acid based process. The alkaline stannate, flouborate, and sulfate chemistries are most often encountered in job shops. The alkaline stannate process typically consists of a heated steel tank, while the sulfuric acid based process uses a plastic or pvc lined steel tank and has filtration. The alkaline process produces a mat, pure tin deposit that has excellent solderability, while the sulfate process produces mat or bright deposits with lesser or marginal solderability but superior appearance. The alkaline process is a bit more difficult to operate than the sulfate process. The alkaline bath is favored for barrel plating applications, although the flouborate bath can also be used.

Compositions (oz/gal) and operating conditions are:

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Alkaline Stannate (g/L):

	Rack	Barrel
Potassium Stannate	100	200
Potassium Hydroxide	15	22
Potassium Carbonate	22-100	22-100
Additives:	None	None
pH	>14	>14

Note: 2 to 4 g/L of cyanide is sometimes added to reduce the effects of metallic contaminants.

Operating Conditions:	
Temperature:	150-180 deg F
Anodes:	Tin
Current Density:	1-100 ASF
Agitation:	Cathode Rod
Filtration:	No
Color of Solution:	Pale yellow or white/clear
Odor of Solution:	No specific
Life:	Many Years

Fluoborate Tin Solutions (rack/barrel plating) (g/L)

Tin (from concentrate)	30-45
Fluoboric Acid	200-250
Boric Acid	22-40
Additives	As Recommended, but required
pH	<.1

Operating Conditions:	
Temperature:	90-120 deg F
Anodes:	Tin
Current Density:	1-80 ASF
Agitation:	Cathode Rod
Filtration:	Yes
Color of Solution:	Pale yellow
Odor of Solution:	No specific
Life:	Many Years

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Acid Sulfate Tin Solutions (g/L)	
Stannous Sulfate	15-45
Sulfuric Acid	7.5-22
Additives	As Recommended, but required
pH	<1
Operating Conditions:	
Temperature:	55-85 deg F
Anodes:	Tin
Current Density:	1-25 ASF
Agitation:	Cathode Rod
Filtration:	Yes
Color of Solution:	Pale yellow/clear
Odor of Solution:	Sweet
Life:	Many Years

12. TIN-LEAD

Tin-Lead is applied to electronic components that require high solderability. The plating hardware is a typical plating setup with continuous filtration optional. There are two basic chemistries the alloy is plated from; the fluoboric and the (proprietary) sulfonic acid based chemistries. These baths are most commonly found in printed circuit board manufacturing shops and job shops specializing in plating for electronics. The electronics industry uses a "high throw" formulation to allow for plating inside drilled holes. Others use a conventional bath that yield the best solderability. The fluoborate bath is made by mixing liquid fluoborate concentrates with water.

Tin-Lead (Solder) Solutions (g/L)		
	Conventional	High Throw
Tin (from concentrate)	52-60	12-20
Lead (from concentrate)	22-30	8-14
Fluoboric Acid	100-150	350-500
Boric Acid	22-40	22-40
pH	<.1	<.1
Temperature:	70-90 deg F	
Anodes:	Lead-Tin Alloy	
Current Density:	15-25 ASF	
Agitation:	Cathode Rod	
Filtration:	Yes	
Color of Solution:	Pale yellow	
Odor of Solution:	Sweet	
Life:	Many Years	

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ELECTROLESS PLATING PROCESSES

One major drawback to electroplating is the non uniform coating produced, because electric current tends to concentrate on sharp edges, corners and points. Electroless plating processes are used when it is necessary to obtain a very uniform coating on complex geometries, because these processes do not depend upon electricity delivered from a rectifier. As the name implies, the coating is produced without an outside source of current. The reducing electrons are chemically provided.

Some electroless deposits are also more corrosion resistant than their electroplated counterparts. The following are two of the most often applied electroless processes:

A. ELECTROLESS NICKEL

Electroless nickel is applied to numerous complex electronic and industrial components for the high degree of wear resistance and corrosion protection. An example is the sliding plates that "mold" the hamburger patties served in fast food restaurants. Two plates slide against each other forming the cavity that is used to "injection mold" the patty. The plates slide against each other at lighting fast speeds. Electroless nickel is also used in the plating of plastics, to provide the first metallic layer on the plastic to yield conductivity
for subsequent deposits.

The electroless plating process normally consists of two plating tanks and a nitric acid storage tank. Each plating tank contains heating elements, an air sparger, and a recirculating filter. The solution will eventually deposit nickel on everything it contacts, so periodically the tank walls and associated equipment must be stripped with nitric acid (thus the nitric storage tank). The plating solution has a finite life (8-14 "turnovers"), after which, it must be waste treated or disposed of through a commercial disposal firm. The electroless nickel plating solution contains strong chelating agents that interfere with a conventional wastewater treatment system, so they must be treated separately using electrowinning, proprietary treatment methods, or special chemical treatments. The rinsewater from electroless nickel operations is usually segregated and treated separate from other rinsewater.

Nickel-Phosphorus Electroless Solutions (g/L)

Nickel Sulfate:	21	11.8
Acetic Acid	9.3	
Lactic Acid	27	
Molybdic Acid		.009
Propionic Acid	2.2	
Lead Acetate	.001	
1,3 Diisopropyl Thiourea		.004
Sodium Hypophosphite	24	22.3
pH	4.6	5.5
Temperature	95°C	95°C
Life:	Weeks/Months	

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Electroless nickel is typically plated from one of two basic chemistries, yielding either a nickel-phosphorus alloy (most common) or a nickel-boron alloy. Each alloy can be plated from a number of different solutions to yield varying alloy compositions. Shown are typical formulations:

Nickel-Boron Electroless Solution (g/L)

Nickel Chloride	30
Sodium Hydroxide	40
Ethylene Diamine	86ml/L
Sodium Borohydride	0.6
Thallium Nitrate	0.007
Sodium Gluconate	15
Diethyl amine Borane	1.0
Lead Acetate	0.02
pH	13-14
Temperature	90 deg C
Life:	Weeks/Months

B. ELECTROLESS COPPER

The major use for electroless copper is in the manufacture of printed wiring boards. The electroless copper is used to apply a thin coating of copper over the top-side and into the drilled holes of the boards. The drilled holes are initially non-metallic, since the boards are made of epoxy-fiberglass. With the electroless copper the holes become conductive for further plating.

Equipment for electroless copper plating usually consists of a polypropylene or PVC plastic tank and filter. Some baths operate at room temperature, so heating is not required, other require heating. The rinsewater and spent electroless copper often contain chelating or complexing agents, so waste treatment becomes difficult.

A typical composition (g/L) electroless copper solution is.

Electroless Copper Solutions (g/L)

Copper Sulfate	13.8	5
Rochelle salts	69.2	25
Sodium Hydroxide	20	7
MBT	.012	
Formaldehyde	38ml/L	10ml/L
Temperature	50 deg C	25 deg C
Life:	Weeks/Months	

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C. OTHERS

There are numerous other electroless plating solutions in the literature, although they are rarely used. The following solutions may be encountered:

ELECTROLESS COBALT (g/L)	
Cobalt Sulfate	30
Ammonium Chloride	84
Sodium Hypophosphite	20
pH	10
Temperature	95 deg C
Life:	Weeks/Months

ELECTROLESS SILVER (g/L)	
Silver Cyanide	1.34
Sodium Cyanide	1.49
Sodium Hydroxide	0.75
Dimethyl Amine Borane	2
Temperature	55 deg C
Life:	Weeks/Months

ELECTROLESS GOLD (g/L)	
Potassium Gold Cyanide	5.8
Potassium Cyanide	13
Potassium Hydroxide	11
Potassium Borohydride	21.6
Temperature	75 deg C
Life:	Days

TYPICAL POST PLATING OPERATIONS-CHROMATING

After plating, parts are often further treated in various chemical solutions to enhance the appearance or corrosion/tarnish resistance of the plated coating. Examples of such operations include chromate films on zinc, cadmium, and copper plates, and stains produced on copper or copper alloy deposits. Application of lacquers, waxes, and other organic topcoats are also popular post plating methods for improving shelf and service life of parts. Chromate "conversion" coatings are so popular, that almost every zinc and cadmium plating line has chromating tanks and rinses built into it and most all zinc and cadmium plated parts have some form of chromate film on top of the metal deposit.

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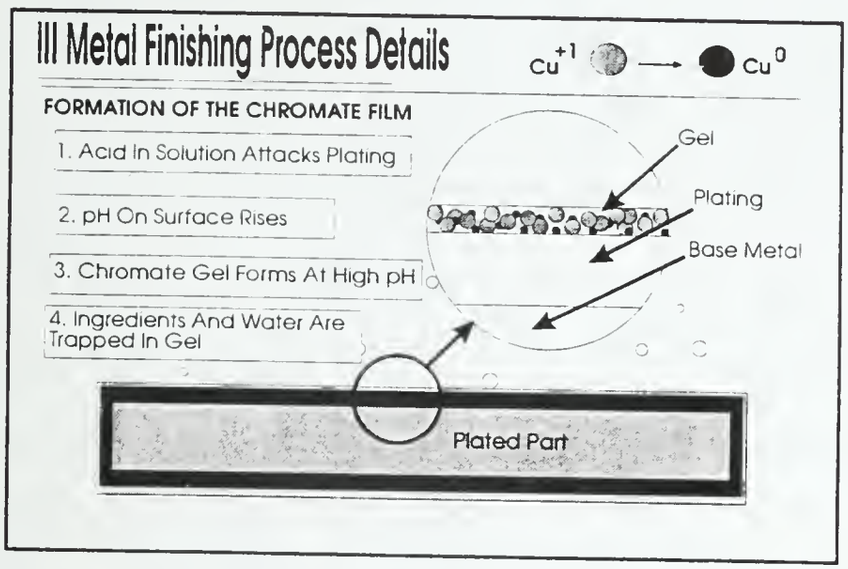
Chromating

A chromate is a very thin complex film created by "converting" a small amount of the top surface of the plated metal into the film, thus the term conversion coating.

The chromate film is formed by immersing the plated deposit into an acidic solution containing a variety of chemicals depending upon the color and corrosion resistance we want to obtain. If, for example, we want the zinc to turn bright, reflective, and with a hint of blue (typically called a blue-bright dip), our solution will contain nitric acid, and potassium ferricyanide, along with some trivalent chromium compounds. If we want a yellow iridescence, hexavalent chromium, in the form of sodium dichromate may be added. If we want olive drab green, even more dichromate along with sulfates may be added. If we want a black coating, a small amount of silver nitrate is added (finely divided silver particles create the black color).


III Metal Finishing Process Details
Cu^{+1} → Cu^{0}
FORMATION OF THE CHROMATE FILM
1. Acid In Solution Attacks Plating
2. pH On Surface Rises
3. Chromate Gel Forms At High pH
4. Ingredients And Water Are Trapped In Gel
Gel
Plating
Base Metal
Plated Part

In each case, the mechanism for forming the chromate film is the same: The plated metal is attacked by the acid in the chromate dip releasing hydrogen as a byproduct of the attack. As the hydrogen is released from the metal surface, the pH of the solution near the metal surface rises high enough to "deposit" a film of metal hydroxides and other trapped ingredients from the solution. The film at first is a delicate gel, but quickly hardens into a thin coating only a few millionths of an inch thick (or less).

The chromate film protects the plated metal from corrosion by acting as a barrier layer against corrosive atmospheres. In general, the more hexavalent chromium trapped in the film, the higher the coloration, and the better the corrosion resistance.

Since the chromate functions by attacking and dissolving some of the plated metal, eventually the solution becomes so contaminated with plated metal, that it stops producing acceptable coatings. At this point the chromate becomes "spent" and must be waste treated.

Rinses following chromating operations are not recoverable (since recovery would only hasten the demise of the chromating solution) and therefore must be routed to a

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wastewater treatment system before discharge to sewer.

Notes:
There are several variations on the chromating process, including some films that are applied with reverse current and others that are applied and then "leached" to remove the coloration. The most commonly applied chromates are the blue brights, followed by the yellow and then the black. The military favor the olive drab for the color and high corrosion resistance.

A significant amount of research is being made into substitutes for chromates that do not contain hexavalent chromium and recycling methods, although not much is on the market at this time.

Some operations utilize a "bright dip" after zinc or cadmium plating. This dip can be used by itself or before chromating. It provides no additional corrosion protection, but enhances the appearance of the deposit by brightening the surface, which has a slight "haze" in the as-plated condition.A bright dip solution is simply a very dilute solution of nitric acid (0.25-0.50% vol) and water. The bright dip removes a thin organic film from the surface of freshly plated zinc or cadmium, rendering the deposit far brighter than before. This is not a chromate, nor a true conversion coating.

End Chapter 3

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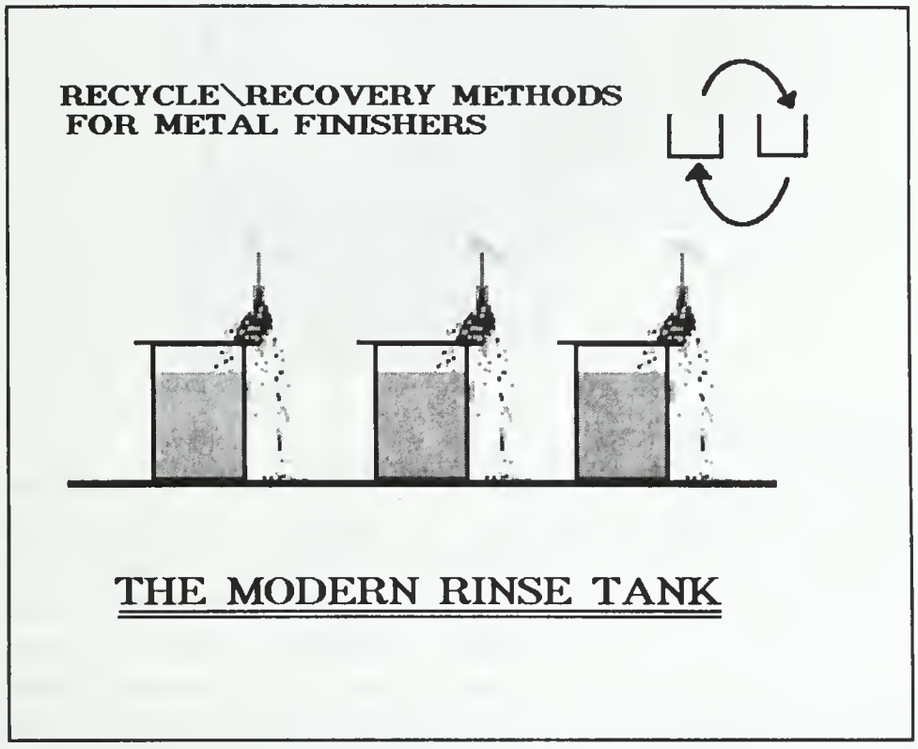
Part IV, Recycle And Recovery in Metal Finishing



REDUCING RINSEWATER USAGE

The more rinsewater that is used by a metal finishing facility, the larger the wastewater treatment system or recovery system will be, the more it will cost, the more difficult it will be to obtain consistent compliance with regulations, and the more chemicals and sludge, will be generated. There is therefore, a great amount of incentive for a metal finisher to reduce the amount of water that is used.

Rinsing processed parts adequately, with a minimum amount of water being used, is a combination of art, and science. An experienced metal finisher will assure that parts are properly drained, that rinsewater flow is at the minimum, and that the process solutions are operated in such a manner that recovery of chemicals dragged out of the process is feasible and optimized.

On the other hand, improper rinsing can lead to increased pollution loading at the wastewater treatment system, contaminated solutions that need treatment or disposal, and extremely high water and sewer bills.

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Factors Affecting Drag-out:

- Solution Viscosity
- Part Geometry
- Drain Time
- Surface Tension

FACTORS AFFECTING DRAG-OUT

The highest effort in pollution prevention practice should be employed at reducing drag-out from metal finishing processes. The quantity of drag-out produced by a process depends upon a number of parameters, some of which are listed here. The higher the viscosity of the process solution, the more liquid adheres to parts leaving the tank and therefore, the higher the drag-out rate. To visualize this, imagine dipping the part in honey and withdrawing it from the vessel. A lot of liquid will "stick" to the part. Now, if the part is dipped in hot butter instead, the liquid will run off in tiny rivulets and droplets, leaving little liquid behind. That is the concept of viscosity. In plating, the viscosity of the process solution is determined by the concentration of the ingredients. By running process baths with lower concentrations, we reduce viscosity and drag-out. The more complicated a part geometry is, the higher the drag-out, because drilled and blind holes trap liquid and carry it out of the process.

The drain time is related to the drag-out for the first 15-20 seconds. During this interval, liquid is running from the parts and hopefully, back into the process tank. By draining for at least 15 seconds, we optimize the drain time and reduce drag-out. Reducing surface tension may or may not reduce drag-out. Experiments have shown that in certain solutions, reducing surface tension (by adding wetting agent) may actually increase drag-out. You need to experiment to find out if this will work for you.

The concentration of ions that tend to form insolubles affects drag-out adversely also. The higher the concentration of ions such as sulfates, silicates, phosphates, and carbonates are in a solution, the higher the drag-out tends to be.

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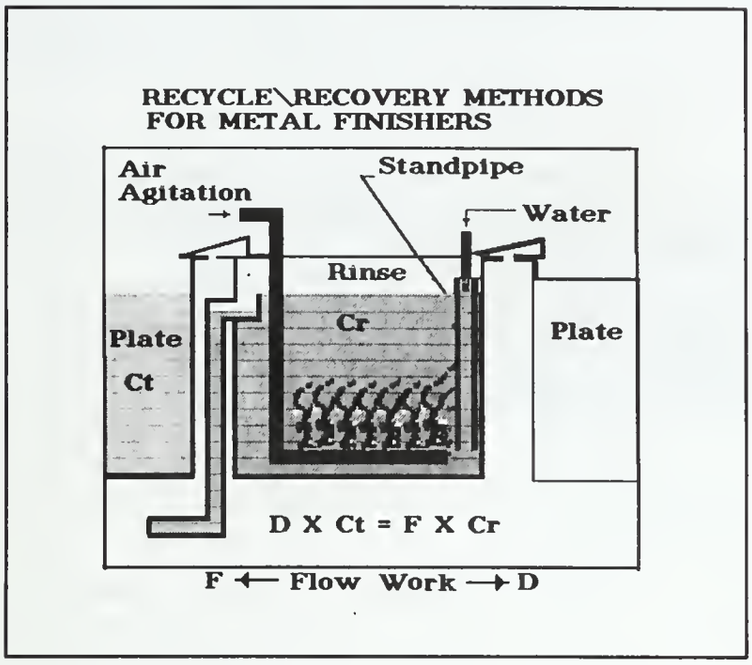

THE SINGLE RINSE

A rinse tank should only be big enough to contain the largest part that is anticipated to be processed. Other features of a modern rinse tank include a skimmer to float off oil, a recirculating pump, prop mixer, or air agitation sparging system, and an entry pipe that creates a sweeping flow of water from the bottom to the top (not important if agitation is high enough).

The flow of water needed to obtain a certain concentration of contaminant in the rinse can be calculated from the following equation for an "ideal" single rinse:

$$D \times Ct = F \times Cr$$

Where:

D is the drag-out rate (gal/hr or liters/hr)
Ct is the contaminant concentration in the process tank (ppm)
F is the rinse flow rate (gal/hr or liters/hr)
Cr is the concentration of the contaminant in the rinse tank (ppm)

For example, if a single rinse is used after a nickel plating tank (Ct = 75,000 ppm of nickel metal) and the drag-out rate is 0.5 gallons per hour, and we want a maximum of 5 ppm nickel in our rinse tank, then we would need:

$$F = \frac{0.5 \times 75{,}000}{5} = 7{,}500 \text{ gallons/hr}$$ of rinsewater flowing in the tank.

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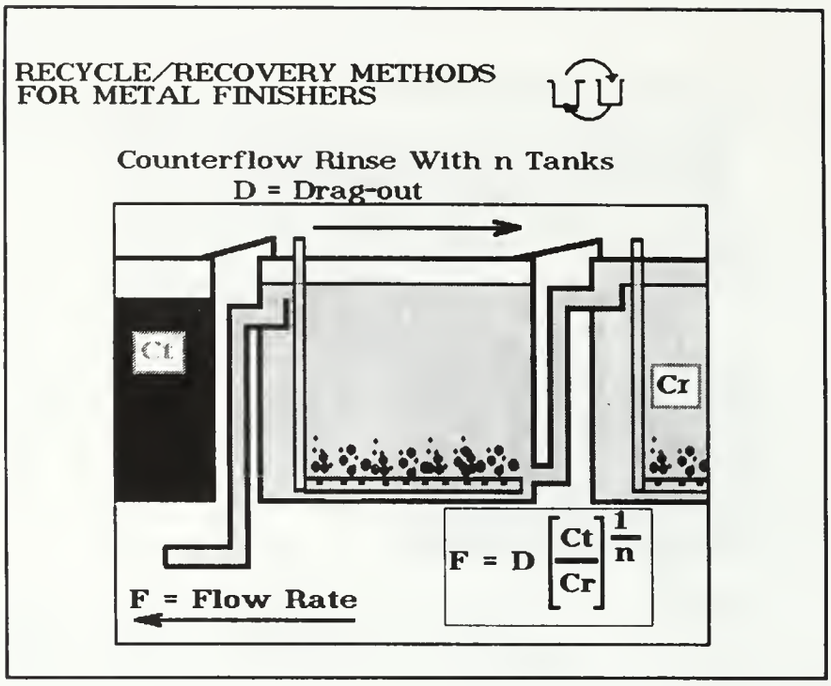

COUNTERFLOW RINSING

To reduce the quantity of water required to obtain a low contamination level in the rinse prior to the next process, a counterflow rinse system can be employed The term counterflow originates from the fact that the rinsewater flows in a direction counter to the work flow. An ideal counterflow rinse can be described by the equation:

$$F = D\,(Ct/Cr)^{1\backslash n}$$

Where n is the number of separate rinse tanks in the counterflow system.

COMPARISON

Single Rinse vs 2 Tank Tank Counterflow

D = 0.5 gph, Ct = 75,000 ppm, Cr = 5 ppm

Single Rinse

$$F = \frac{0.5 \times 75{,}000}{5} = 7{,}500 \text{ gph}$$

2 Tank Counterflow

$$F = 0.5\left[\frac{75{,}000}{5}\right]^{1/2} = 61.25 \text{ gph}$$

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Here is a comparison of the amount of water it would take with a single rinse, vs a two tank counterflow rinse, to achieve a rinse concentration of 5 ppm, if the dragout rate is 0.5 gal/hour and the concentration in the process tank is 75,000 ppm.

If a three tank counterflow was used, the flow rate required to achieve 5 ppm in the last rinse would be only 12.33 gal/hour!

While counterflow rinses are wonderful for reducing water consumption, they do have drawbacks. For example, it is difficult to use counterflow rinses after acidic solutions that attack coatings, such as chromates, because the additional acid attack that may occur in the rinse tank(s) can yield poor chromate films that don't meet specifications. Also, the first tank in a counterflow rinse system can get so concentrated, that it needs to be ventilated just as if it were a process tank.

On manually operated lines, it is often difficult to convince personnel to use each compartment of a counterflow rinse, since that is extra work effort. Skipping compartments can result in rinse tanks containing too high concentrations of contaminants and may result in the loss of a process solution due to contamination.

HOW DIRTY CAN THE RINSEWATER BE?

ppm	Preceding	Following
7500	Alk Cln	Alk Tin Plate
750	Alk Cln	Acid Plate
750	Acid Pickle	Acid Plate
375	Sulfuric	Chrome Plate
50	Acid Pickle	Cyanide
25	Chrome Plate	Dry

Note: Above are just guidelines, NOT to be taken Verbatim

It is impossible to provide truly useful rinse concentration levels to use in the equations provided earlier, because each plant must deal with different base metal alloys, different part geometries, and different processing chemicals. The above data is therefore to be used only as a guide. Each plant must make calculations based upon their own information and drag-out rate variability.

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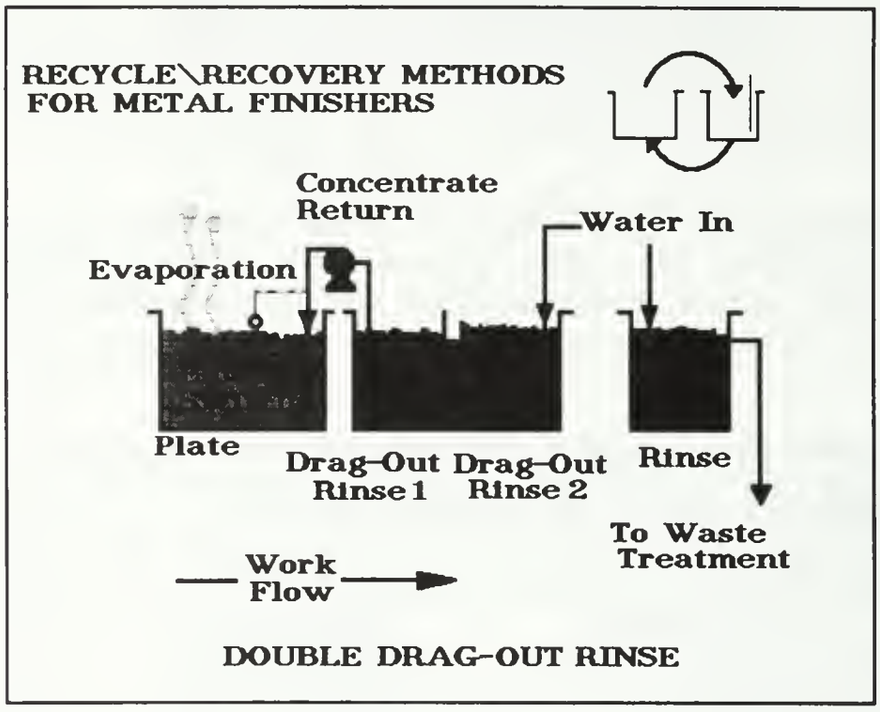
If the process tank has a recovery device such as an evaporator, the rinse tanks must be kept significantly "cleaner" because impurities will be recycled to the process and can eventually cause rejects. Analytical history on the process can be helpful in determining the rate at which impurities build up, so that purity targets for the rinses can be established. For similar reasons, all rinses prior to and after recovery systems should utilize deionized water exclusively. If tapwater is used, all ions typically in tapwater, such as calcium, magnesium, iron, sulfate, phosphate, carbonate, silicate etc. will accumulate in the process solution.



DRAG-OUT RINSES

The most commonly used method to reduce the dragout rate from a process tank is to employ a dragout rinse tank. A typical dragout rinse tank consists of a tank equipped with a pump that discharges to the process tank. The drag-out rinse is filled with deionized water and as evaporation in the process tank allow s, the rinsewater in the drag-out tank is returned to the process tank along with whatever chemistry it collected.

The efficiency of the process can be increased by utilizing two rag-out tanks in series, as shown in the slide. Operators can get into trouble when drag-out rinses are not efficiently returned to the process tank. If you wait too long, the drag-out tank becomes almost as concentrated as the process tank and the drag-out tank is useless. There is an optimum amount of time that the operator can wait before returning the drag-out solution back to the process tank. This optimum time must be calculated, based on the worst case of drag-out and then the return schedule must be adhered to. If evaporation losses from the process are too low, drag-out tanks

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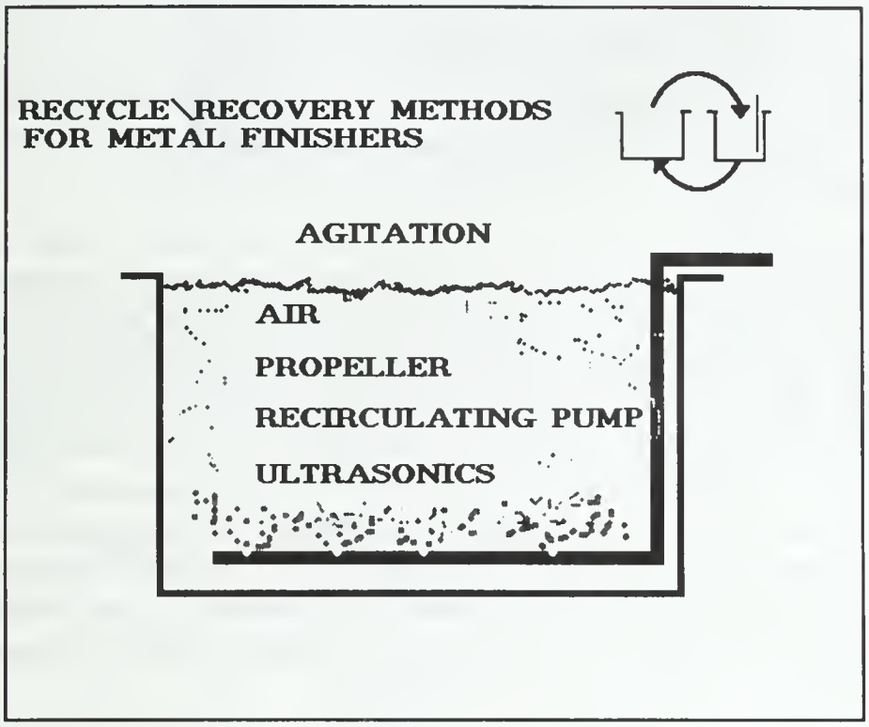
become useless, unless auxiliary evaporation can be installed. Drag-out tanks after strong acid tanks are also essentially useless, if the additional time the part is in the relatively strong acid in the drag-out tank causes rejects.



RINSE TANK AGITATION

Because the modern rinse tank runs at very low rates of flow, agitation of the rinsewater becomes very important. Without agitation, soils accumulate in the corners of the rinse tanks and rinsewater can become stratified into layers. Shown here are several methods of rinse tank agitation. The most popular method is air sparging, using low pressure air blowers. A typical air agitation rate is 2cfm of air per square foot of rinse tank surface area (length times width). Air sparging is most popular because it is the easiest method of agitation to install, is low in cost, and does not consume valuable tank space (except for the sparger at the bottom). However, air agitation normally does not do an effective job of eliminating dead zones in a tank. You can normally see dirt in the corners of air agitated tanks. You can even get into OSHA trouble by air agitating the concentrated first rinse of certain counterflow rinses!

By physically moving the rinsewater through use of a recirculating pump or prop mixer, all dead zones are eliminated and mixing is at peak efficiency. Prop mixers pose safety hazards (unless a safety ring is welded to the prop) and take up space within the rinse tank (pumps do too). They also consume more energy to operate. Ultrasonics are sometimes added to rinses in aerospace applications, where the sonication removes debris that may be trapped in crevices or blind holes. Ultrasonics in rinses for improvement of mixing the rinsewater is difficult to justify by economics alone.

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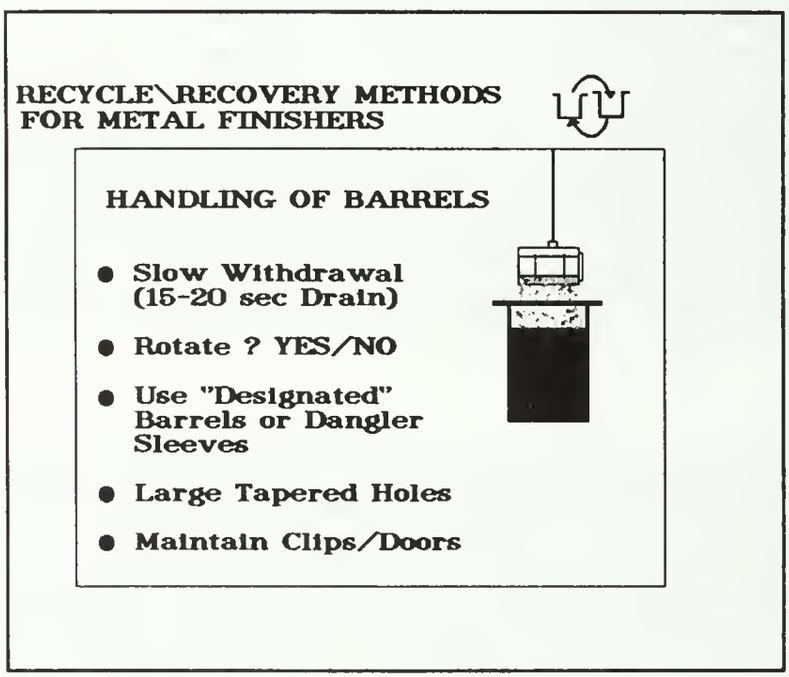
CONTROLLING WATER FLOW

- Turn Valves Back
- Restrictors
- Timers
- Conductivity Controllers
- Flow Meters

CONTROLLING WATER FLOW

Rinsewater should only be flowing when the rinse tank contains water that is too dirty for the next process tank. Therefore, a significant amount of water can be wasted if the rinse tank is allowed to flow continuously. While several methods of controlling water flow are listed here, experience has shown that flow restrictors and conductivity controls yield the most success. Conductivity controller probes are very sensitive to contamination by floating oil/debris. Some manufacturers offer probes that work on an "inductive loop" principle. These probes can be coated with oil or grease and still read conductivity accurately. Fixed orifice flow restrictors cost less money and are very effective in limiting water usage to the prescribed amount, but they don't turn the water off when it is not needed. Over time, the orifice will become larger than designed, so they need to be replaced and monitored periodically.

If your work flow is sporadic and production rates are low (10 parts per day, for example), counterflow rinses may be a waste of floor space and money. In such cases, single rinses with conductivity controls should work equally well, at less cost.


RECYCLE\RECOVERY METHODS
FOR METAL FINISHERS
HANDLING OF BARRELS
● Slow Withdrawal (15-20 sec Drain)
● Rotate ? YES/NO
● Use "Designated" Barrels or Dangler Sleeves
● Large Tapered Holes
● Maintain Clips/Doors

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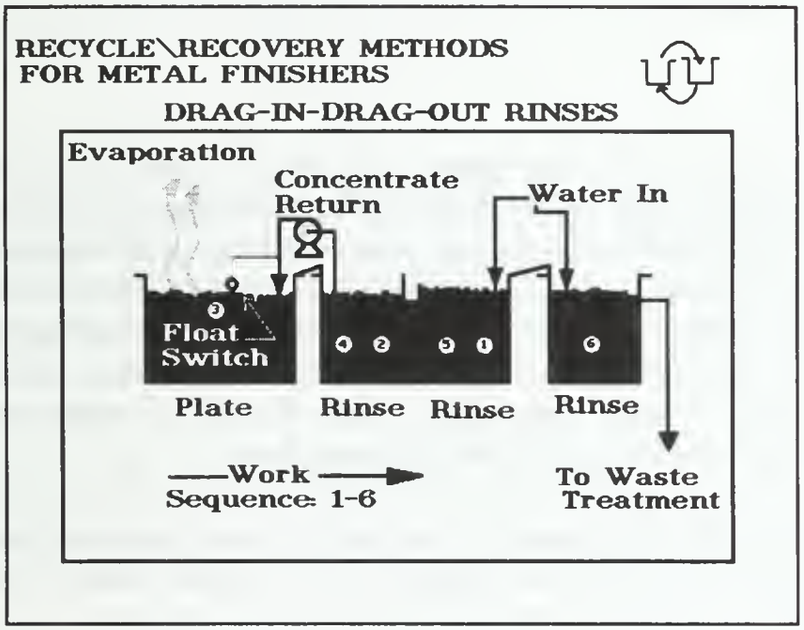
RINSING BARRELS

Rinsing barrels properly to reduce drag-out and rinsewater flow requirements is extremely important, because the drag-out rates of barrels is very high (usually 1/4 gallon of drag-out per barrel). Barrels should be slowly withdrawn from the process tank to allow for at least 20 seconds of hang time for proper draining. If the barrel contains cup shaped parts, it should be rotated while it is held above the process tank, otherwise rotating the barrel may actually **increase** drag-out. Some innovative metal finishers utilize designated barrels for cleaning/pickling and then transfer to other barrels designated for plating. The result is that the dangler stays metal free, and does not contaminate the cleaners and acids with heavy metals. Angler sleeves, when properly used do the same thing, without having to use designated barrels.

The plating barrel should have the largest holes that will still hold the parts within the barrel, to facilitate draining and improve plating efficiency. Holes tapered from the outside in drain better than straight wall holes. Also, the doors and clips need to be maintained to prevent parts from falling out and contaminating process and rinse tanks.



DRAG-IN-DRAG-OUT TANKS

A dragout tank is beneficial because it captures chemicals that are ordinarily discharged to waste treatment and returns them directly to the process tank in the most usable form. Platers often ignore an additional benefit that can be obtained by entering the dragout tank with the work **before** going into the process tank. This routinely returns drag-out solution to the process tank. This is extremely useful for processes that operate at room temperature, such as cyanide zinc plating. Theoretically, a well operated drag-in-drag-out system will reduce chemical losses from the process by 50%. This system can also be used for acid dips and cleaners. One disadvantage is the added labor on manually operated lines. Another disadvantage is that the system can not readily be incorporated into existing automated lines.

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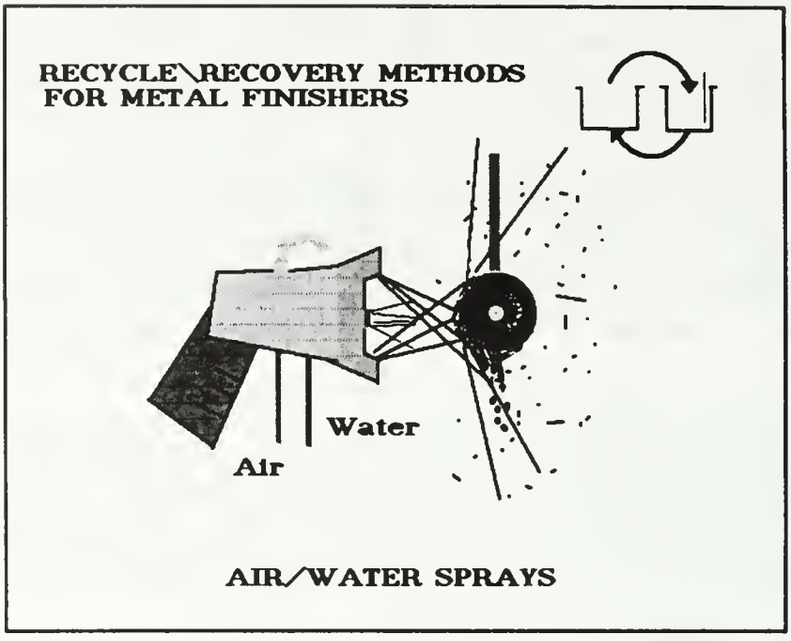

AIR-WATER SPRAYS

A plant faced with a severe water shortage recently reduced water consumption in their hand plating lines by 99%. They replaced all their running rinses with empty tanks (no drains) and high pressure spray guns similar to paint spray guns. These guns sprayed a lot of air and very little water. The line operators would hold the processed parts inside the tank and spray rinse them for a few seconds. The compressed air was quite useful for rinsing blind holes and crevices. With designated rinse tanks and deionized water, there would be great possibility for almost total recycle in manually operated process lines.

Disadvantages that must be considered include the need for high purity compressed air, added labor, and the possibility of OSHA violations created by the mist generated.

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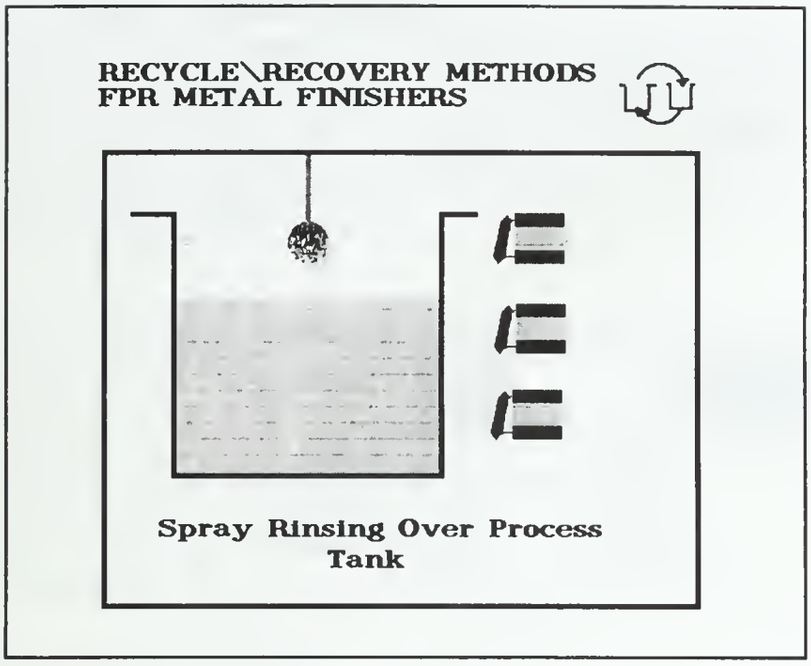

SPRAY RINSING

Properly designed and functioning spray rinses mounted at the top of a process tank can reduce chemical losses from hot processes dramatically. We emphasize hot because spray rinses add whatever water they spray to the process tank. Spray rinses are essentially useless for processes that operate at temperatures below 100 deg. F.

The design of the spray system is crucial to its success. The nozzles must be made of materials that resist the chemicals in the tank. Furthermore, the spray nozzles should be easy to clean, because they clog often. They should also utilize as little water as possible to do the job. Spray nozzles are available for spraying most ny pattern desired, ranging from conical to a flat fan. Chose the spray pattern that will result in the most surface area being contacted by the spray for your part geometry. This may require some experimentation. A rule of thumb says that if 60% of the part surface is contacted by the spray, spray rinsing will be effective. For best efficiency, sprays should be operated on an automated basis, as parts leave the process. Enough freeboard should be designed into the tank, so that impingement of the spray onto the parts does not increase fugitive emissions from the process and create a health hazard.

Clogging of spray nozzles will be minimized, if deionized or RO water is sprayed. Air knives, also located just above the process tank, can reduce the volume of dragout by forcing the solution dragged out back to the tank. The air used by air knives must be clean and high in humidity, to prevent drying of residual process solution onto the parts.

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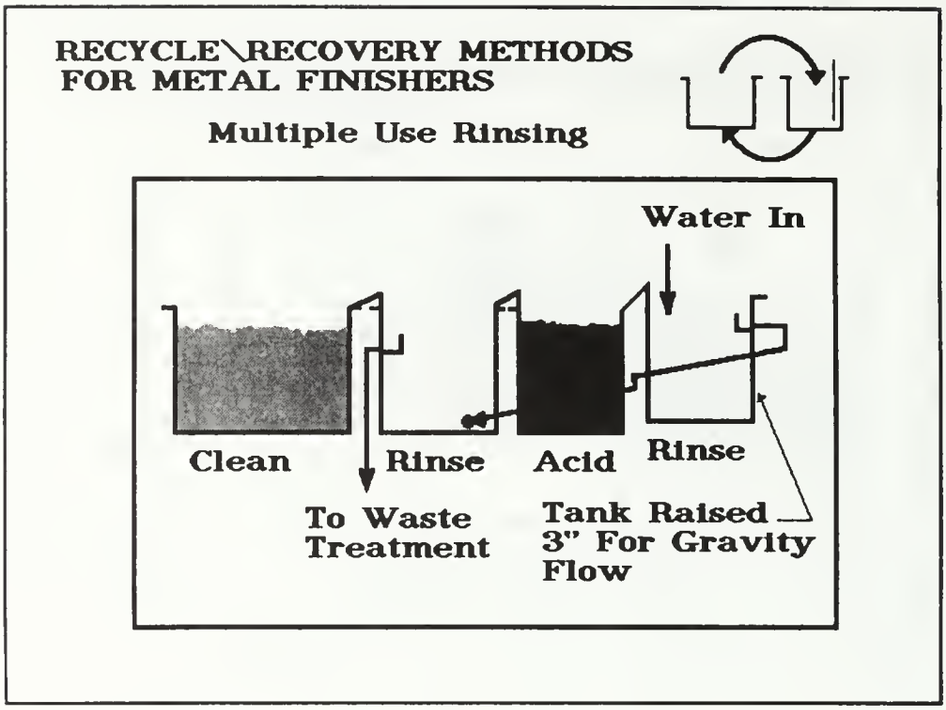

MULTIPLE USE RINSING

Why not use rinsewater that contains "compatible" contamination over again for another process rinse? If this is possible, then water consumption would be drastically reduced. In reality, this IS possible. For example, why not allow rinsewater after an acid dip to actually flow by gravity to the rinse tank after electrocleaning. Besides using half the amount of rinsewater, rinsing is actually improved by the neutralization that will occur between the acid and the alkali from the two rinses. A very large plant in the south was able to utilize this concept to reduce water usage from 500 gpm to 54 gpm, without sacrificing any of their quality.

This concept for rinsewater use reduction is extremely useful in cleaning, pickling, and passivating lines. The major drawback is that the rinsewater that is re-used must be compatible with the parts and the chemicals in the subsequent process. For example, you can not run the rinsewater after chromating to the rinse ahead of chromating because in-adherent chromate films would form on the parts, while they are in the rinsewater. Another drawback is the fact that tanks must be elevated about 2-3" for the water to flow by gravity. This can then result in tank lines getting progressively taller down a process line, but this usually is not a big problem.

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WHAT CONSTITUTES DILUTION?

1. No wastewater treatment in Metal Finishing Facility
2. Routing "Clean" Water to Sewer
3. Phony "Treatment"

WHAT DOES NOT CONSTITUTE DILUTION?

1. Flows that go to Treatment
2. Batches of concentrated wastes that are partially treated and then routed to secondary treatment 3. Dilution of a concentrated waste prior to treatment

WHAT CONSTITUTES DILUTION?

Dilution used for the purposes of obtaining an effluent that is in compliance with Federally mandated discharge regulations, is against the law. Dilution is practiced when:

1. A company performs little or no waste treatment, and runs enough water in their rinse tanks or other processes to meet discharge concentration limits.

2. Rinse tanks are operated at flow rates far above those necessary to protect subsequent processes.

3. A company routes non contact cooling water or other "clean" non-regulated process water directly to sewer or to a process or rinse tank that drains to the sewer without going through a pretreatment operation.

4. A company routes "clean" process water to a "sham" treatment system operated in addition to the real pretreatment system.

WHAT DOES NOT CONSTITUTE DILUTION?

The following are not considered dilution:

1. Using a high rinsewater flow, if all flow is routed to waste treatment. In such cases, the metal finisher is paying extra for wasted water and treatment chemicals, and he might be affecting the performance of the pretreatment system, but he is not diluting.
2. Treatment of a concentrated waste by batch, then routing the treated waste through the pretreatment system at low flow in order to obtain secondary treatment.

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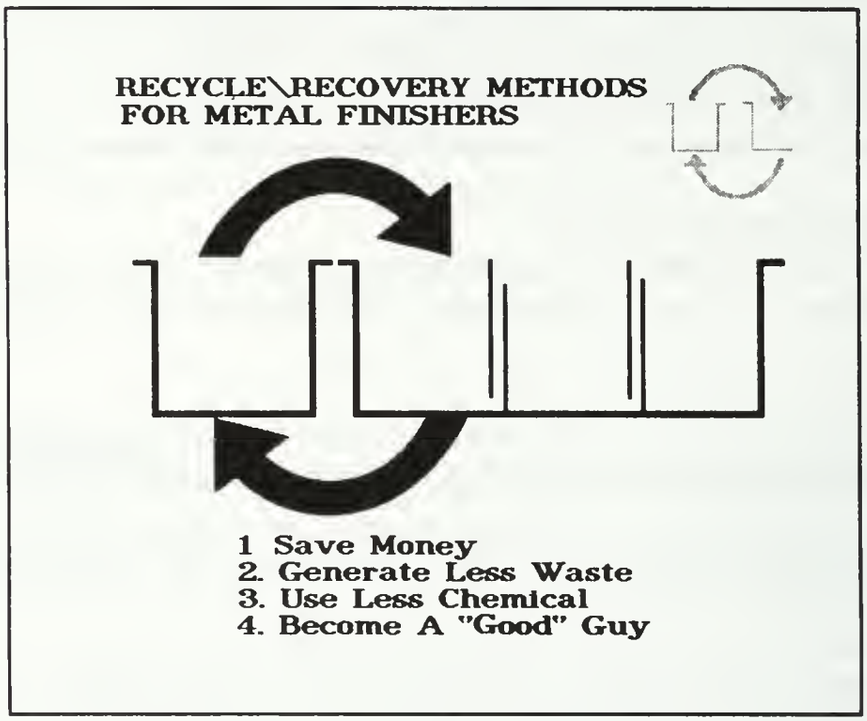
3. Dilution of a concentrated spent process solution prior to treatment, as required to ensure safety and proper treatment (some are dangerous to treat when concentrated).

MATERIAL RE-USE AND RECOVERY



RECYCLE/RECOVERY METHODS

Once rinsewater flow rates have been reduced to a minimum, the metal finisher can review his processes and determine what, if any, recycle/recovery methods will reduce his pollution loading to the wastewater treatment system. Recycle/Recovery systems can reduce the amount of solid waste (F-006 filter cake) generated, and can often yield savings in chemical costs that in some cases can pay for the equipment and installation in a short time.

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WHAT IS RECYCLE / RECOVERY?

1. Material is re-used to make product
2. Material is substitute for product
3. Material is returned to process with no prior "Reclaim" operation

WHERE MAY YOU FIND IT BEING EMPLOYED?

1. Recycle concentrates to processes
2. Recovery of metals from rinses
3. Sale of metal bearing wastes
4. Regeneration of process baths
5. Recycle of treated wastewater

WHAT IS RE-USE/RECYCLING?

Direct re-use involves the re-use of a waste material without processing it either as a feed stock in a production process or as a substitute for a commercial product. Reclamation or recovery removes impurities and recovers raw material or by-products.

Solid Wastes are recycled when they are:

- Used or re-used in an industrial process to make a product.
- Effective substitutes for commercial products
- Returned to the original process without being first re-claimed

Technologies used for re-claiming are dictated by the type of waste and nature of contamination, and fall into two basic categories:

1. Physical Separation

This makes use of differences in physical properties such as:

- Density
- Particle Size
- Boiling/Freezing Point
- Solubility

2. Chemical Separation

This makes use of chemical reactions to effect removal of selected constituents in a waste. Examples:

- Precipitation
- Oxidation/Reduction
- Ion Exchange
- Electrolytic Recovery

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WASTES PRODUCED IN METAL FINISHING OPERATIONS

Primary wastes are derived mostly from:

1. Dumping of process solutions and related materials (cleaners, acids, activating solutions, chromates, and stripping solutions)

2. Rinse water used to reduce the concentration of processing chemicals to a safe level for the next process step

Other wastes are from maintenance operations and accidents such as spills, overflows, filter maintenance.

Areas of metal finishing Operations Where Reuse/Recovery Technologies are possible include:

OPERATIONS WHERE YOU MAY FIND RECYCLE/RECOVERY:
- Recycling concentrates to process baths through rinse tanks.
- Nonrecycle recovery of metals or concentrates.
- Selling By-product sludges
- Regenerating Process Baths
- Recycling Treated Wastewater

Reuse/Recycling Technologies in the Metal Finishing Industries

Some of the more commonly used reuse/Recycling Technologies in the metal finishing industry are:

- Evaporation
- Electrolytic Recovery
- Ion Exchange
- Reverse Osmosis

Less commonly used reuse/recycle methods in Metal Finishing are:

- Carbon Adsorption
- Crystallization
- Electrodialysis

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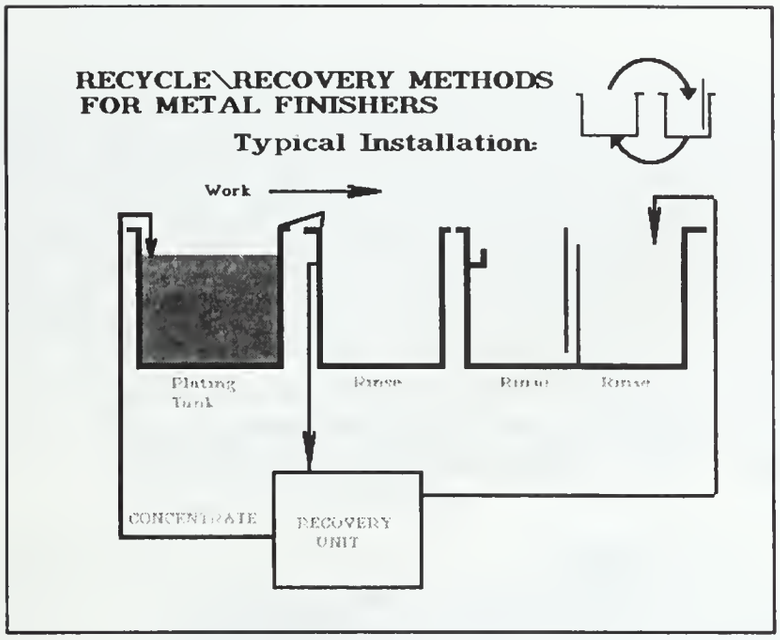
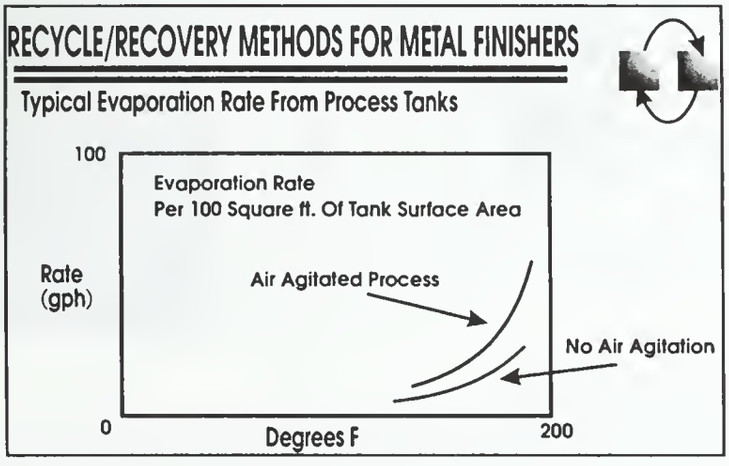


A typical recycle/recovery system for a metal finishing process tank involves either a drag-out tank, a counterflow rinse, or a combination of both. The water used in the rinses should be de-ionized to protect the process solution from buildup of dissolved minerals from tap-water. Such buildup can slowly make a process solution contaminated to such an extent that it can become a total loss. The recovery "unit" operates off either the drag-out tank, or the first rinse in the counterflow rinse tank. There are numerous variations, but this is most often the case. The recovery system may recover a part or all the chemicals in the process drag-out, depending upon the technology. The rinsewater and any non recovered discharge from the recovery system continues to flow to the wastewater treatment system.



A. EVAPORATIVE RECOVERY

Evaporation of water from processes that operate at elevated temperature can be very significant and increase dramatically, as the solution temperature goes beyond 140 deg. F, or if the solution is air agitated. The evaporation rate is also dependent upon the relative humidity in the air. For example, at 140 degrees, and 50%

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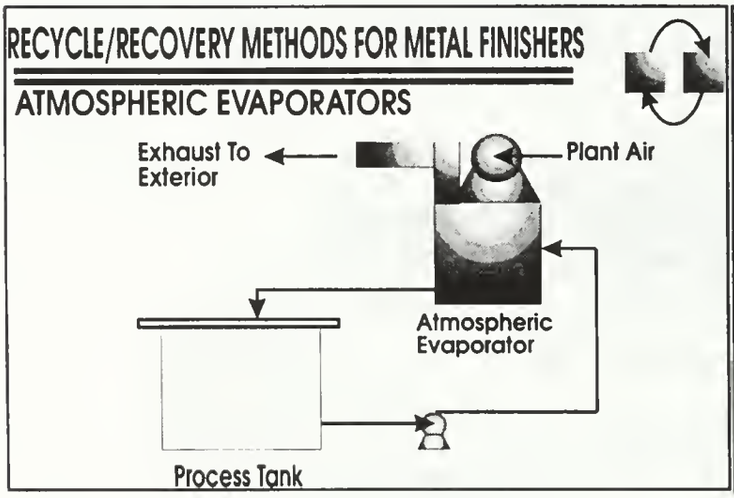
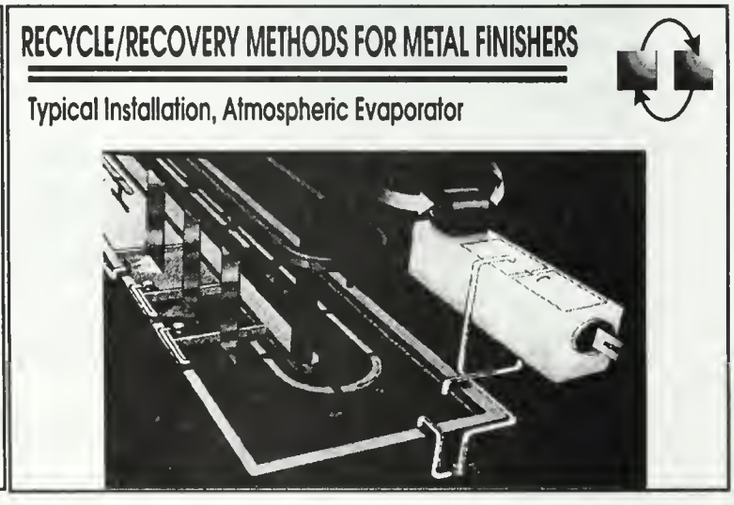
relative humidity, an air agitated tank, with 100 square feet of surface area may evaporate 10 gallons of water per hour, while a non air agitated tank evaporates only 4 gal/hour. At 160 degrees, the same numbers are estimated at 20 and 10 gal/hour, respectively. This evaporative loss creates "room", in the process tank, to return a portion of the drag-out loss. This can be accomplished in several ways, including simply manually returning the drag-out liquid to the process tank. When the drag-out rate is high, however, there will not be enough room in the process tank to efficiently return the dilute drag-out solution. An evaporator can then be used to either create the additional room in the process tank, or to concentrate the rinsewater so less volume goes back to the process tank.

Evaporators are commonly employed on chromium, nickel and cyanide copper plating operations, although they are not limited to just these. Evaporators fall into two general categories; vacuum and atmospheric. Vacuum evaporators recover a concentrated process solution and condensed water (distillate) that can be re-used as rinsewater, while atmospheric evaporators recover only the process concentrate. There is a significant cost difference between the two evaporation systems, with atmospherics typically costing around 10% that of vacuum systems. A common misconception is that atmospheric systems use "free" energy. However, if they use "plant air" that has been heated, they indirectly consume a significant amount of energy. In hot, dry climates, atmospherics can be operated using "free" thermal energy, but still require electricity for the pumps and blower.





ATMOSPHERIC EVAPORATORS

These devices operate by spraying the dilute waste stream over packing media, grid, or plates, and then blowing plant air over the packing, to effect evaporation. Advantages include low cost and simple maintenance. A major drawback is the inability to evaporate on days when air humidity levels approach 80-90%. In areas of general high humidity, the solution to be evaporated will need to be heated to some degree. Atmospheric evaporators generally have low capacities, ranging from 10-40 gal/hour, although they

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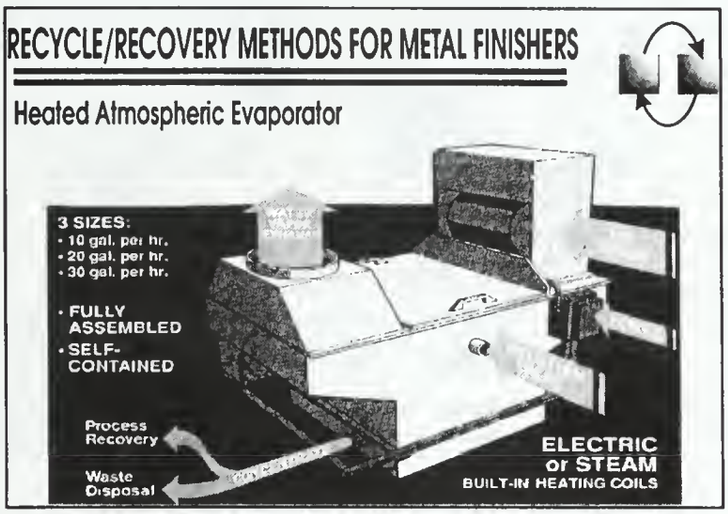
can be installed in "series" to attain whatever rate is necessary (as long as dry air is available). On cyanide solutions, atmospherics can aggravate carbonate buildup in the plating bath due to carbon dioxide adsorption from the entrained air. This will then generate waste, from the carbonate removal process. It can be very difficult to use atmospheric systems on process solutions containing wetting agents, because large volumes of foam can be generated.



At least one manufacturer has offered an atmospheric evaporation system that includes heating elements to improve evaporative efficiency on high humidity days.

VACUUM EVAPORATORS

There are a number of different evaporator designs on the market, normally differing in how the vacuum is achieved (eductor, vacuum pump), or how much energy is employed (single effect, double effect), or how much vacuum is achieved. The higher the vacuum, the lower the temperature at which water will boil. By boiling the water off at lower temperatures (110-130 deg F), the vacuum evaporators protect some delicate ingredients of processing solutions that might decompose at higher temperatures. Advantages of these systems include recovery of both a concentrate and condensed water, and operation in all weather conditions. Disadvantages include high energy and maintenance costs, and foaming of some process solutions (one evaporator manufacturer has a design that can handle foam).

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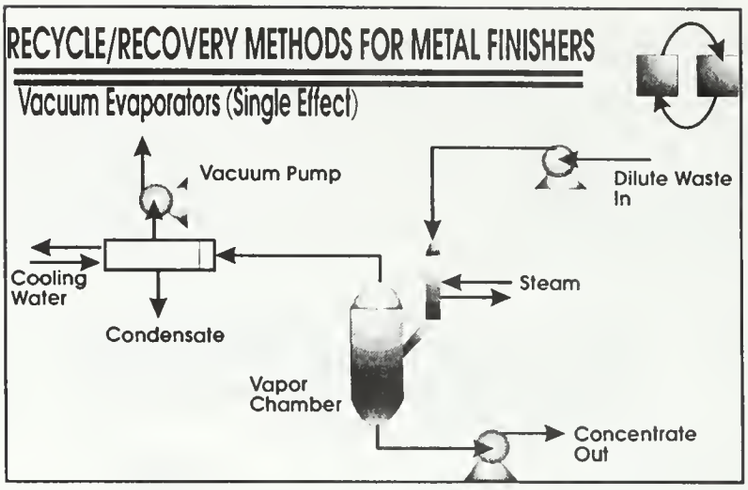
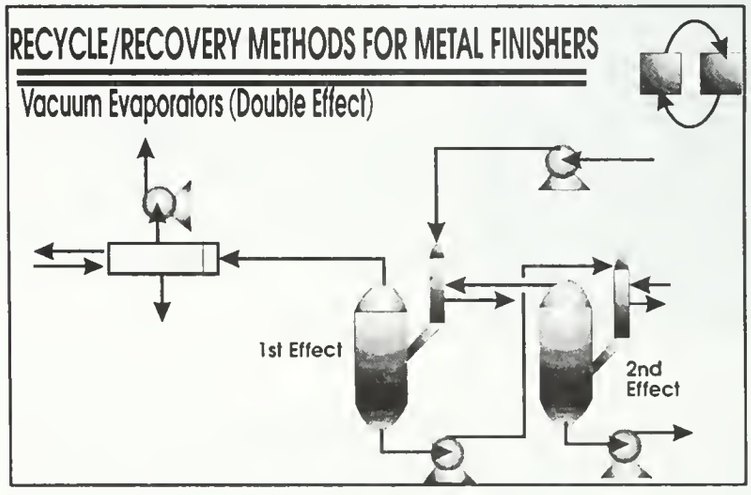


SINGLE EFFECT EVAPORATOR

A single effect unit usually uses steam to heat the liquid to its boiling temperature. The steam is passed through a steam coil or jacket, and the vapors produced by the boiling liquid are drawn off and condensed. The concentrated liquid is then pumped from the bottom of the vessel. The process requires about 1200 BTU/lb of water evaporated. There are a variety of designs on the market, including evaporators made out of glass, stainless steel, and carbon steel.

Vacuum system designs generally vary in the method(s) used to develop a vacuum, some using vacuum pumps, while other utilize eduction systems. In general, the higher the vacuum achieved, the lower the boiling temperature of the dilute waste stream, but the higher the energy, maintenance, and equipment costs. Cyanide solutions concentrated at lower temperatures do not tend to form carbonates to the same degree as with atmospherics.

Vacuum evaporative systems consume considerable energy, and the condensing system requires cooling water (which becomes heated and can be used elsewhere in the plant).



MULTIPLE EFFECT EVAPORATORS

A multiple effect unit consists of a series of single effect evaporators. Vapor from the first evaporator is used as the heat source to boil liquid in the second evaporator. Boiling

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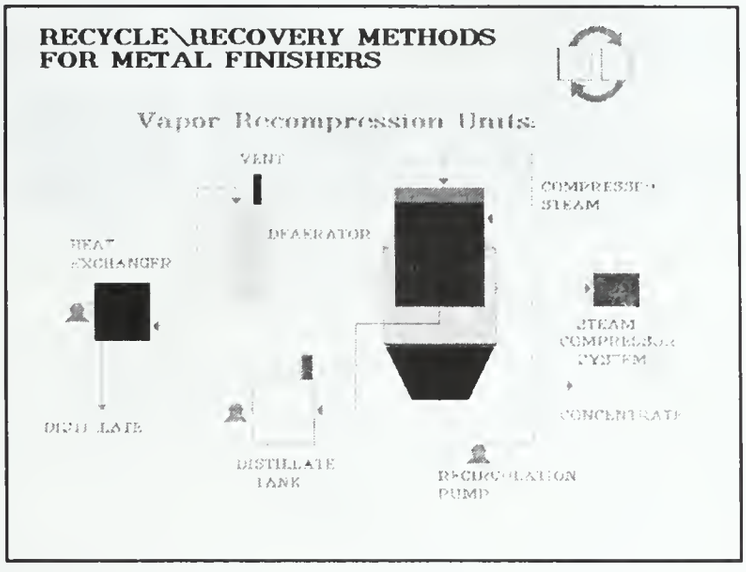
is accomplished by operating the second evaporator lower than the first. The process can continue for several evaporators (effects). Depending on the number of effects, multiple effect units can require as little as 200 BTU/lb of water evaporated.



VAPOR RECOMPRESSION UNITS

The vapor recompression evaporators use steam to initially boil the liquid. The vapor produced is compressed to a higher pressure and temperature. The compressed vapor is the directed to the jacketed side of the evaporator instead of using more steam, and is thus used as a heat source to vaporize more liquid. These units require as little as 40 BTU/lb of water evaporated.

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The following data on evaporative systems was generated in a research project (Project 71) conducted by AESF (prices are 1980).

ECONOMICS OF USING EVAPORATIVE RECOVERY TECHNIQUES

Solution	Est. Recovery (Kg/Day)	Method	Value ($/yr. 1987)
Chromium Plating Rinse	13	Vacuum	15,100
Chromium Plating Rinse	85	Vacuum	98,756
Zinc Plating Rinse	100	Vacuum	45,210
Chromium Plating Rinse	75	Vacuum	87,120
Chromic Acid Etch	275	Vacuum	319,440
Chromic Acid Etch Rinse	21	Vacuum	24,374
Chromic Acid Etch Rinse	95	Vacuum	110,352
Nickel Plating Solution	34	Atmospheric	86,020
Chromium Plating Rinse	45	Atmospheric	52,272

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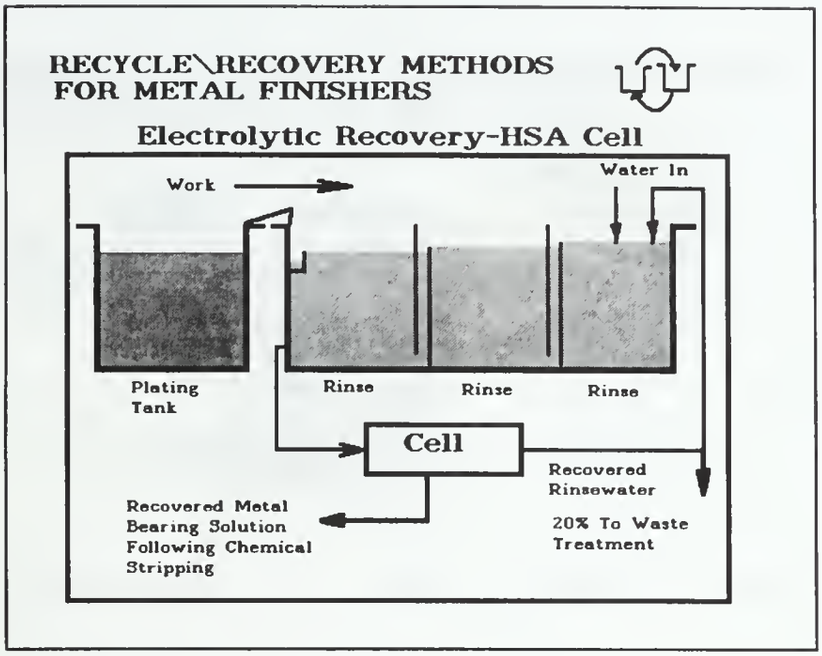

ELECTROLYTIC RECOVERY

This is a technology that uses special electroplating equipment to lower the concentration of dissolved metals in drag-out rinses and concentrated rinse tanks. Benefits include reduction of sludge generation, some electrolytic destruction of cyanide, and reuse or sale of scrap metal plated out. Disadvantages include incomplete recovery (some waste is generated), tendency to spontaneous combustion of plated metal, and energy costs. Electrolytic systems fall into two primary categories:

a. Equipment for primarily removing metal from the wastewater stream, in a form that has little recycle potential.

b. Recovery of metals with recycle of some other ingredient potential

The major difference between these systems is the type of cathode use to plate the metal out of the wastewater. A "conventional" system might be "home made", and simply use corrugated steel or stainless steel electrodes. A high surface area cathode system that improves the efficiency of metal remove is available from one supplier. Another supplier offered an "HSA" (high surface area) reactor that plated out cadmium from a drag-out rinse and simultaneously destroyed cyanide by electrolytic oxidation. The manufacturer is no longer in business, but the systems are still available on the used equipment market.

Typical applications of these systems include after-acid-copper plating, cyanide cadmium plating, cyanide zinc plating, and cyanide copper plating. While attempts have been made to utilize these systems on nickel plating processes, the lack of a suitable insoluble anode has held back most progress.

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ECONOMICS OF USING ELECTROLYTIC RECOVERY

Solution	Estimated Recovery Rate	Recovery Technique	Reuse Application	Metal Value ($/kg)	Recovered Metal Value ($/yr)
Acid Zone Concentrate from Ion-Exchange (2.5 g/L Zn)	5 kg/week	LSA	As Anodes	1.37	343
Nickel Plating, Drag-out	23 kg/week	LSA	As Anodes	10.12	11.638
Copper Plating, Off-line Drag-out	0.35 kg/week	LSA	Sold	1.81	32
Cadmium Plating, Drag-out	0.7 kg/week	LSA	Sold	3.52	123
Acid Copper Plating, Drag-out	23 kg/week	HSA	Sold	1.81	2,082
Acid Zinc Plating, Drag-out	16 kg/week	LSA	As Anodes	1.37	1,096
Bright Nickel Plating, Drag-out	30 kg/week	LSA	As Anodes	10.12	15,180

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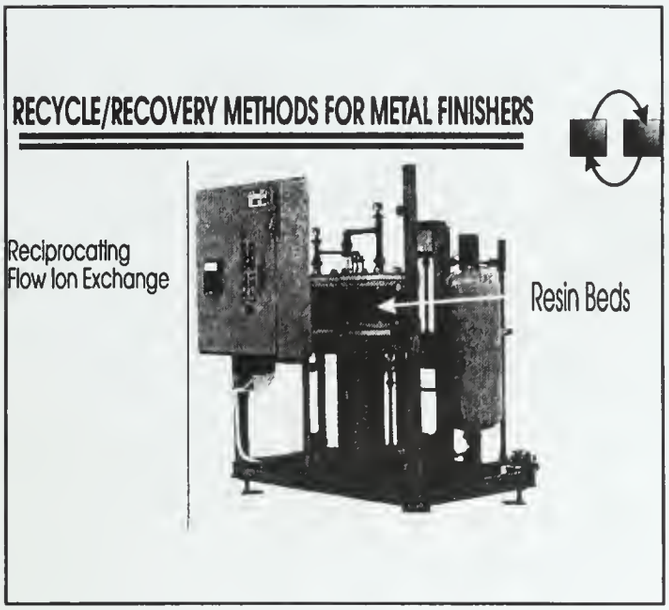

ION EXCHANGE

Ion exchange has been in use in the metal finishing industry for decades. One "centralized recovery" facility in Minnesota utilizes ion exchange cylinders to remove dissolved metals and cyanide from rinsewaters. The cylinders are rotated, and returned to the central facility, where they are treated to either recycle beneficial materials, or are waste treated. A typical metal finishing ion exchange system has a fixed bed of resin with the ability to exchange or remove cations or anions such as chromates from rinsewaters. Ion exchange is almost totally unaffected by the flow rate at which it is used, however, highly concentrated inflows should be avoided, except for systems specifically designed for such inflows.

The resins used for metals recovery typically are co-polymers consisting of styrene and divinyl benzene in cationic or anionic form. In general, divalent and trivalent ions are easier than monovalent ions, to remove using ion exchange.

When the useful capacity of the ion exchange column is exhausted, it is regenerated using dilute acid (sulfuric or hydrochloric) for cationic resins, and sodium hydroxide solution for anionic resins. Some cationic exchange systems us dilute acid followed by a solution of sodium hydroxide. The hardware of pre-packaged units consists of pressure vessels ranging from 2-6 feet or more in diameter, handling flow rates up to 300 gpm. Custom made units, with 12 foot diameter columns, have been built to handle flows as high as 1150 gpm. The loading typically is 10 gpm per square foot of resin cross section. The chief advantage of ion exchange, is that it is selective in what it removes. In a recycling application, that means that you don't recycle all the impurities along with the beneficial material (this is not 100% true). Some resins (weak acid cationic) require close control of the pH of the feed stream, with lower pH reducing the capacity of the resin, and higher pH tending to clog the resin with solids (metal hydroxides). The systems also have the drawback of not having suitable instrumentation to tell when the resin is saturated. Saturated resin will discharge an effluent containing high concentrations of the pollutant it is supposed to remove.

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ECONOMICS OF USING ION EXCHANGE FOR RECYCLE/RECOVERY

Solution	Estimated Recovery Rate	Recovery Technique	Reuse Application	Metal Value ($/kg)	Recovered Metal Value ($/yr)
Chromic Acid Etch Rinse	45 kg Cr/day	Ion Exchange Evaporation (Vacuum)	Process Solution	3.52	52,272
Hard Chrome Plating Rinse	151 kg Cr/wk	Ion Exchange Evaporation (atmospheric)	Process Solution	3.52	26,576
Sulfuric Acid Pickle Solution	275 tons/year	Ion Exchange	Process Solution	0.09	25.865
Nickel Plating Rinse	130 kg $NiSO_4$ /wk	Ion Exchange Evaporation (vacuum)	Process Solution	1.76	11,440
Chrome Plating Rinse	45 kg Cr/wk	Ion Exchange Evaporation (vacuum)	Process Solution	3.52	9,715
Acid Zinc Plating Rinse	10 kg Zn/wk	D.H. Ion Exchange Electrolytic	Sold	1.37	685
Chrome Plating Rinse	85 kg Cr/wk	Ion Exchange Evaporation (atmospheric)	Process Solution	3.52	14,960
Chrome Plating Rinse	18 kg Cr/wk	Ion Exchange	Process Solution	3.52	3,168

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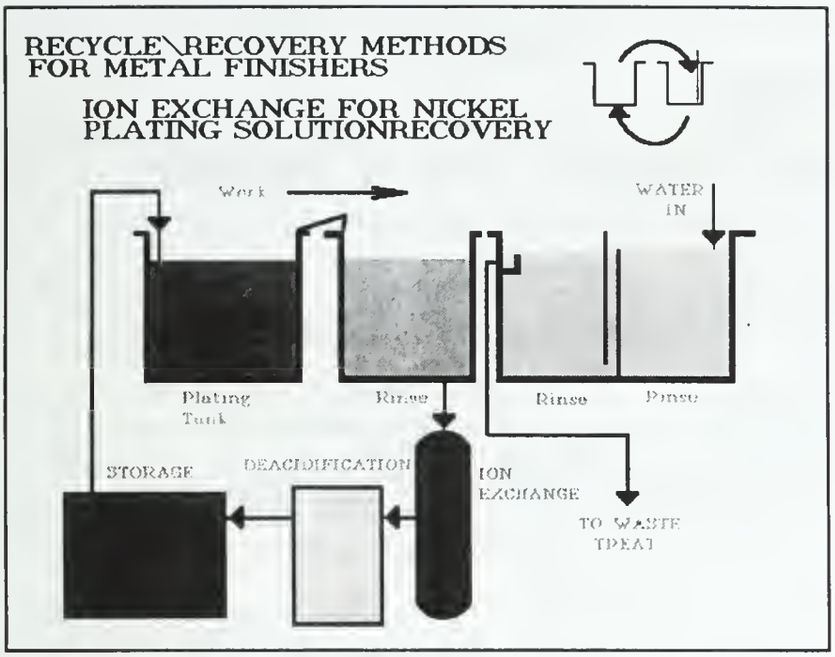

Additional disadvantages include the requirement of additional treatment equipment for modifying the regenerant stream to a chemistry suitable for re-use. An example is a nickel recovery system, which requires de-acidification of the regenerant before it can be used in the plating bath. The regenerant stream is not highly concentrated (2-4 oz/gal is typical), and ancillary operations such as de-acidification require waste treatment of the excess acid. The technique is considered to be an expensive recovery method that requires a lot of care and knowledge of operation.

Ion exchange also can be used to remove specific ions from rinsewater at the rinse tank. A typical application may be to remove nickel, copper (from an acid bath) or chromium from their respective rinses and then to return the regenerated metal ions to the plating bath as concentrates.

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Resin Types

Strong Acid Cation

$2(R\text{--}SO_3H) + NiCl_2 = (R\text{--}SO_3)_2Ni + 2HCl$ **(1)**

Wide pH Range, H or Na Form, Large Vol. Regenerant

Weak Acid Cation

$2(R\text{--}COOH) + NiCl_2 = (R\text{--}COOH)_2Ni + 2HCl$ **(2)**

pH > 6, H Form, Less Acid Required For Regen.

Strong Base Anion

$R\text{--}NH_3OH + HCl \rightarrow R\text{--}NH_3Cl + HOH$ **(3)**

Wide pH Range, Neutralize Acid, Large Vol Regenerant

Weak Base Anion

$R\text{--}NH_2 + HCl \rightarrow R\text{--}NH_3Cl$ **(4)**

pH < 7, Low Alkalinity, Small Vol Regenerant

Heavy Metal Selective Chelating

$2(R\text{-}EDTA\text{-}Na) + NiCl_2 = (R\text{-}EDTA)_2Ni + 2NaCl$ **(5)**

Similar to Weak Acid Cation But Highly Selective

Resin Types

Ion exchange resins are classified as cation exchangers, which have positively charged mobile ions available for exchange, and anion exchangers, whose exchangeable ions are negatively charged. Both anion and cation resins are produced from the same basic organic polymers. They differ in the ionizable group attached to the hydrocarbon network. It is this functional group that determines the chemical behavior of the resin. Resins can be broadly classified as strong or weak acid cation exchangers or strong or weak base anion exchangers.

Strong Acid Cation Resins.

Strong acid resins are so named because their chemical behavior is similar to that of a strong acid. The resins are highly ionized in both the acid ($R\text{--}SO_3H$) and salt ($R\text{--}SO_3Na$) form. They can convert a metal salt to the corresponding acid by the reaction shown in the slide.

The hydrogen and sodium forms of strong acid resins are highly dissociated and the exchangeable $Na+$ and $H+$ are readily available for exchange over the entire pH range. Consequently, the exchange capacity of strong acid resins is independent of solution pH. These resins would be used in the hydrogen form for complete deionization; they are used in the sodium form for water softening (calcium and magnesium removal). After exhaustion, the resin is converted back to the hydrogen form (regenerated) by contact with a strong acid solution, or the resin can be converted to the sodium form with a sodium

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chloride solution. For Equation 5, hydrochloric acid (HCl) regeneration would result in a concentrated nickel chloride (NiCl2) solution.

Weak Acid Cation Resins.
In a weak acid resin, the ionizable group is a carboxylic acid (COOH) as opposed to the sulfonic acid group (SO3H) used in strong acid resins. These resins behave similarly to weak organic acids that are weakly dissociated.
Weak acid resins exhibit a much higher affinity for hydrogen ions than do strong acid resins. This characteristic allows for regeneration to the hydrogen form with significantly less acid than is required for strong acid resins. Almost complete regeneration can be accomplished with stoichiometric amounts of acid. The degree of dissociation of a weak acid resin is strongly influenced by the solution pH. Consequently, resin capacity depends in part on solution pH. A typical weak acid resin has limited capacity below a pH of 6.0, making it unsuitable for deionizing acidic metal finishing wastewater.

Strong Base Anion Resins.
Like strong acid resins, strong base resins are highly ionized and can be used over the entire pH range. These resins are used in the hydroxide (OH) form for water deionization. They will react with anions in solution and can convert an acid solution to pure water Regeneration with concentrated sodium hydroxide (NaOH) converts the exhausted resin to the hydroxide form.
Weak Base Anion Resins. Weak base resins are like weak acid resins, in that the degree of ionization is strongly influenced by pH. Consequently, weak base resins exhibit minimum exchange capacity above a pH of 7.0 These resins merely absorb strong acids; they cannot split salts. The weak base resin does not have a hydroxide ion form as does the strong base resin. Consequently, regeneration needs only to neutralize the absorbed acid. Less expensive weakly basic reagents such as ammonia (NH3) or sodium carbonate can be employed.

Heavy-Metal-Selective Chelating Resins
Chelating resins behave similarly to weak acid cation resins but exhibit a high degree of selectivity for heavy metal cations. Chelating resins are analogous to chelating compounds found in metal finishing wastewater; that is, they tend to form stable complexes with the heavy metals. In fact, the functional group used in these resins is an EDTA compound. The resin structure in the sodium form is expressed as R-EDTA-Na.
The high degree of selectivity for heavy metals permits separation of these ionic compounds from solutions containing high background levels of calcium, magnesium, and sodium ions. A chelating resin exhibits greater selectivity for heavy metals in its sodium form than in its hydrogen form. Regeneration properties are similar to those of a weak acid resin; the chelating resin can be converted to the hydrogen form with slightly greater than stoichiometric doses of acid because of the fortunate tendency of the heavy metal complex to become less stable under low pH conditions. Potential applications of the chelating resin include polishing to lower the heavy metal concentration in the effluent from a hydroxide treatment process, or directly removing toxic heavy metal cations from

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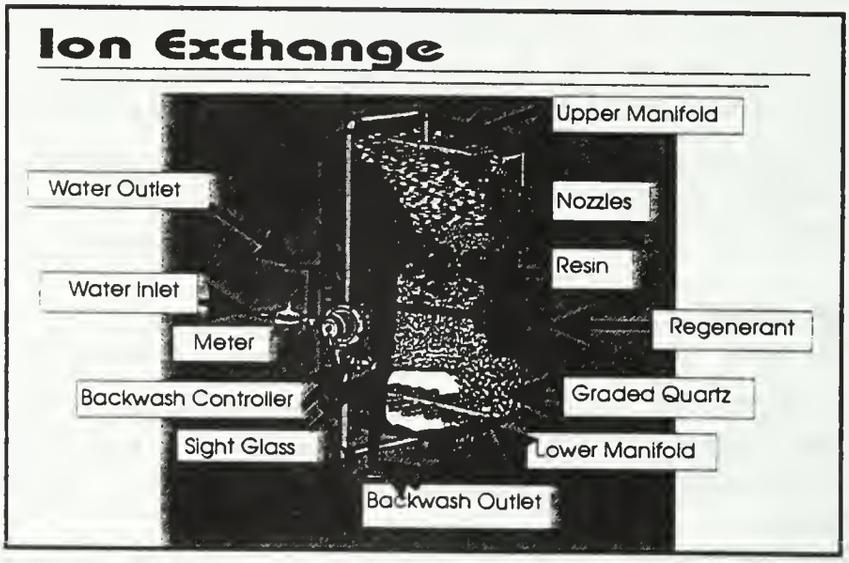
wastewaters containing a high concentration of nontoxic, multivalent cations.



Ion Exchange Process Equipment and Operation
Most industrial applications of ion exchange use fixed-bed column systems, the basic component of which is the resin column. The column design must:

- Contain and support the ion exchange resin
- Uniformly distribute the service and regeneration flow through the resin bed
- Provide space to fluidize the resin during backwash
- Include the piping, valves, and instruments needed to regulate flow of feed. regenerant, and backwash solutions

End-of-Pipe Systems
Ion exchange can be used in two different ways for end-of-pipe pollution control. The process has been demonstrated as a means of polishing the effluent from conventional hydroxide precipitation to lower the heavy metal concentration further, and it has been used to process untreated wastewaters directly for removal of heavy metals and other regulated pollutants (not recommended, except in special cases).

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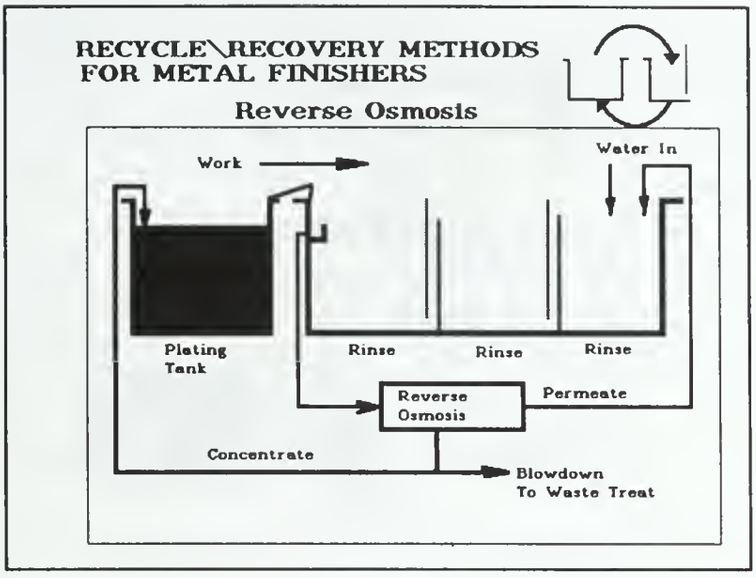
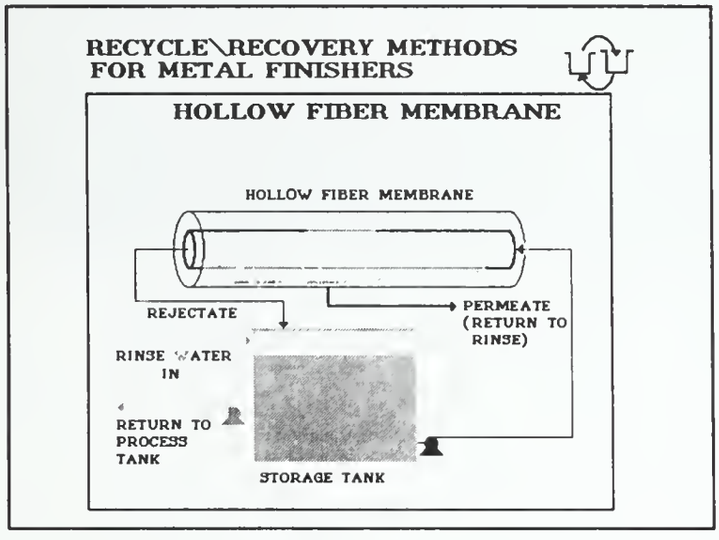


REVERSE OSMOSIS

Reverse osmosis (commonly called "RO"), is used to separate water from inorganic salts, through the use of a "membrane" that allows transfer of water and "rejects" the salts. The system utilizes pressures of 400-800 psi, generated by pumps to force the water through the membrane ("permeate"), leaving a concentrated residual liquid ("rejectate") behind. To prevent fouling of the membrane, feed solutions must be pre-treated to remove materials such as manganese, calcium, lead, iron, carbonates, particulates, oils, and other fouling materials.



The membranes are made out of cellulose acetate (similar to the clear plastic covering cigarette packages), aromatic polyamides, and cross linked polyamides. They come in various configurations, including "spiral wound", "tubular", and "hollow fiber". The tubular membrane is inserted onto or into the surface of a porous tube. This type of RO is used for low volume (low pressure) applications. The spiral wound membrane is a flat sheet separated by a mesh spacer that is spirally wound around a perforated plastic tube that acts to channel the permeate flow. The hollow fiber membrane consists of millions of membrane fibers.

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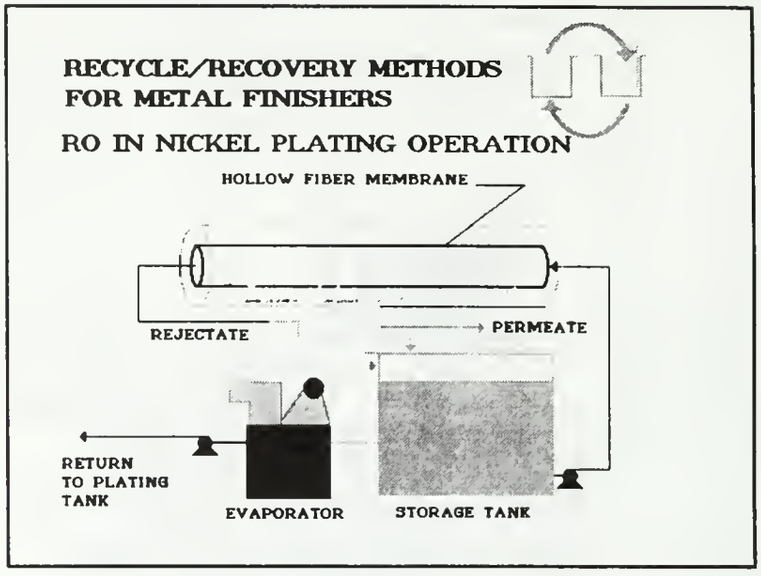

The most common (99%) of all recycling applications of RO is on the rinsewater of a nickel plating tank. The rejectate is often too dilute to directly return to the tank, so evaporation is often added to the system. RO systems have been developed to be used on alkaline solutions such as cyanide copper and brass, but the rinse water must be filtered extremely well, and must have a low carbonate level, and the water used in the plating and rinse tanks must be deionized. Aside from the fouling problems, some RO systems are very temperature sensitive. For example, a cellulose acetate membrane can not withstand a temperature greater than 96 deg. F. The membrane also rapidly deteriorates if the pH of the feed stream is less than 3 or higher than 10. Commercial systems that use RO membranes outside this pH range do exist. In such applications, the membrane is designed to be expendable and is more easily and economically replaced.

RO systems are also in use as a polishing operation after wasetwater treatment. The RO system reduced total dissolved solids in the treated waste water, so that the water can be recycled to the process.

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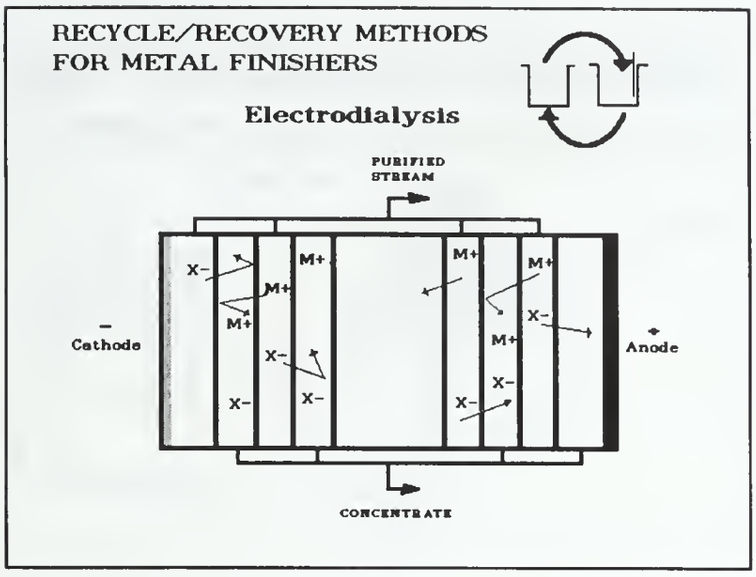

ELECTRODIALYSIS

Electrodialysis (ED) is a process which used a "stack" of closely spaced ion exchange membranes through which ionic materials are selectively transferred or rejected. Driving the ions through the membranes, is an electrical potential applied by a rectifier to two electrodes as shown in the slide. In a plating operation, ED is typically applied to a rinse tank after plating and the ED system separates the dissolved ions from the rinsewater. Because each pass through the system does not create a very concentrated product stream, the system is usually connected to a recirculating drag-out rinse tank. Typical applications are on

drag-out tanks after gold, silver, nickel and acid tin plating tanks. On nickel plating systems, ED does not remove organics from the rinsewater, thereby eliminating organic contaminant buildup that would be obtained with evaporative systems. Disadvantages are the same as those for RO, plus the cost of the equipment (very high).

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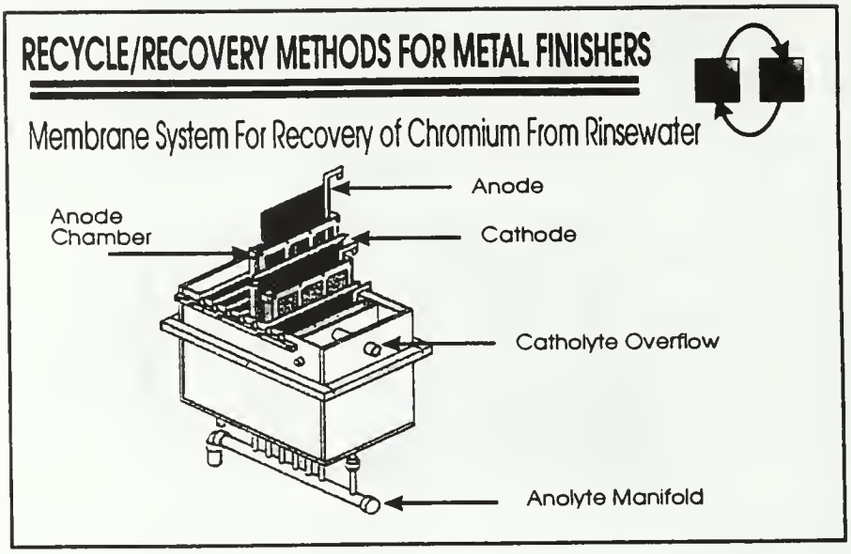
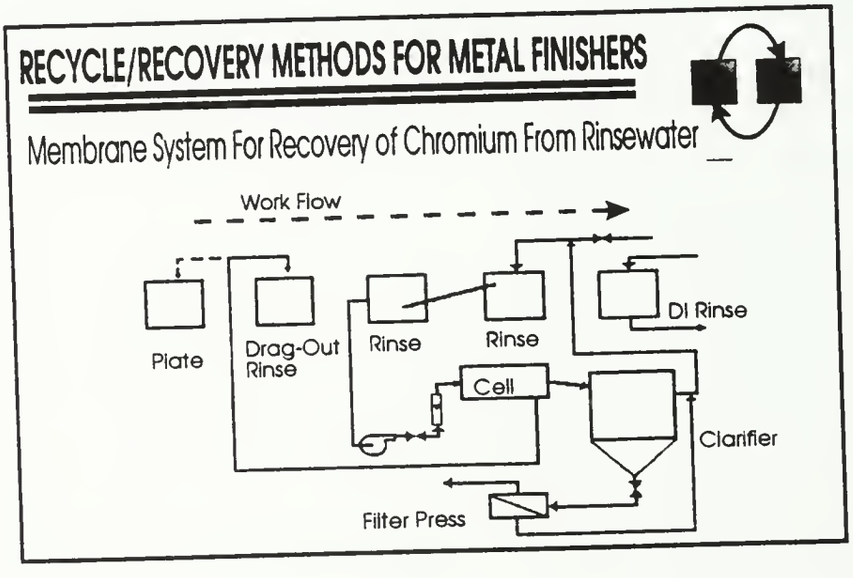


OTHER MEMBRANE/ELECTROLYTIC SYSTEMS

There numerous other membrane based recovery systems on the market. Here is a chromic acid recovery system that uses proprietary membranes and DC current to concentrate chromic acid from rinsewater. Rinsewater is pumped into the catholyte section of the cell and DC current causes the chromate ions which are negatively charged, to migrate through the membrane into the anolyte chamber, where the chromate is concentrated to several grams per liter. The recovered solution is then used for evaporative make-up. Heavy metal contaminants are held back by the membrane and are concentrated in the catholyte section. Liquid from the catholyte section is periodically sent to waste treatment for heavy metals removal. The anodes and cathodes are typically made of lead.



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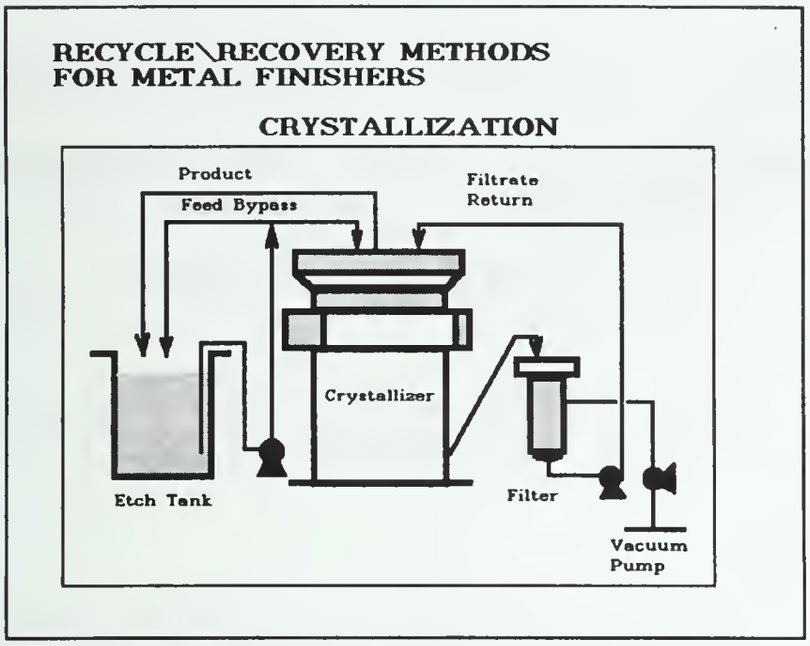

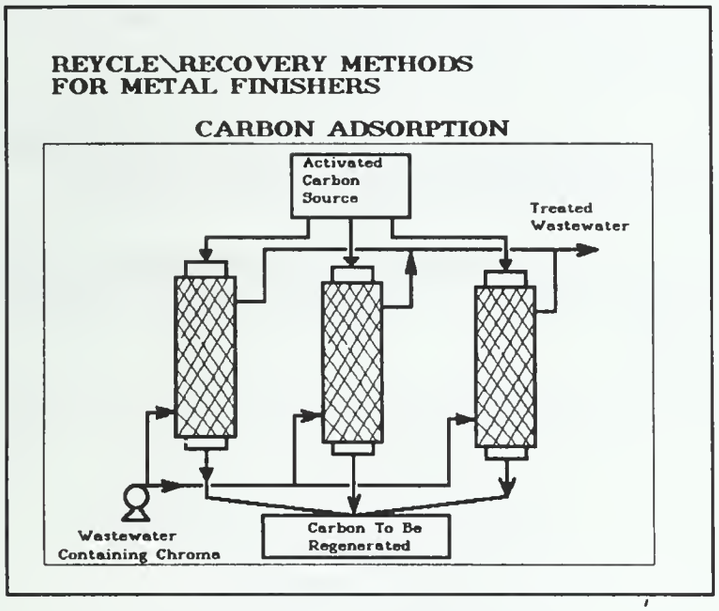

OTHERS

There are a number of other recycle and recovery schemes available to metal finishers. Some, such as crystallization or freeze drying are extremely useful in special applications, but are too expensive for general use in job shops. Others are "black boxes" that work by some mysterious new (and highly questionable) discovery. In all cases the potential user should thoroughly investigate the technology and avoid being a "pioneer".

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Hazardous Waste Minimization Manual for Small Quantity Generators, Center for Hazardous Materials Research, 320 William Pitt Way, Pittsburgh, PA 15238, 1987. (Call I-800-334-CHMR.)

Waste Minimization Opportunity Assessment Manual, United States Environmental Protection Agency, EPA 625/7-88/003, July, 1988 (NTIS)

Waste Minimization Audit Report: Case Studies of Minimization of Cyanide Waste from Electroplating Operations, EPA 600/S2-87/056, January 1988 (NTIS).

Control and Treatment Technology for the Metal Finishing Industry -- In-plant Changes, EPA 625/8-82-008, January 1982. (Write to CERI,Technology Transfer, U.S. EPA, P.O. Box 12505, Cincinnati, OH 45212)

ADDITIONAL POLLUTION PREVENTION INFORMATION CAN BE OBTAINED FROM:

Center For Hazardous
Materials Research (CHMR)
320 William Pitt Way
Philadelphia, PA 15238
(800) 334-CHMR

Pollution Prevention Program
U.S. EPA Region III
841 Chestnut Building
Philadelphia, PA 19107
(215) 592-9800

National Assoc. Of Metal Finishers
111 E. Walker Drive
Chicago, Illinois 60601
(312) 644-6610

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Part V, POLLUTION PREVENTION IN METAL FINISHING

Setting up a good pollution prevention program need not be a difficult or expensive undertaking. The essential preliminary step to any pollution prevention program is a waste audit. The waste audit tracks your hazardous waste by monitoring all of the waste which is produced at your facility to learn where it was generated. This results in a systematic survey of a company's operations and is designed to identify areas of potential waste reduction. The waste audit can be divided into six steps:

WASTE AUDIT STEPS:

- Identify hazardous substances in waste or emissions.
- Identify the sources of these substances.
- Set priorities for various waste reduction actions to be taken.
- Analyze some technically and economically feasible approaches to pollution prevention options.
- Make an economic comparison of pollution prevention options.
- Evaluate the results.

Since pollution prevention is an ongoing effort, waste audits should be repeated at least once a year. Document previous and current pollution prevention activities, evaluate their effectiveness, and implement future actions accordingly.

GENERAL POLLUTION PREVENTION PRACTICE

Many pollution prevention practices are low-cost, low-risk alternatives to hazardous waste disposal. Most of the approaches do not require a great deal of sophisticated technology and can be relatively inexpensive. This and the following sections will introduce you to general approaches to pollution prevention which should be considered in any pollution prevention program.

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Management Initiatives

Commitment/Involvement

1st And Most Important Step

Foster Employee Awareness

Develop/Improve Facility Operating Procedures

Set Goals

Create Incentives

Management Initiatives

Management commitment and involvement is the key element in your pollution prevention program. Being vital to the success of any pollution prevention program, management initiatives should be considered as a preliminary step in your program. Effective management initiatives should foster employee awareness of, and participation in, pollution prevention efforts and developing or improving facility operating procedures to meet pollution prevention goals. Initiatives may include employee training sessions in hazardous material handling and pollution prevention,
developing process documentation, and improving scheduling of processes.

Although pollution prevention commitments should begin with management, the employees are often the best resource for suggesting improvements in the day-to-day operations of the business. Employee incentive programs encourage employees to design and use new pollution prevention ideas.

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Improved Operating Procedures

Material and waste handling and storage improvements are the simplest and often most effective first steps toward reducing wastes. Good operating practices involve the procedural or organizational aspects of a manufacturing process and include the following:

Improved Operating Procedures

- Implement an effective inventory control system to enable you to prevent waste generation due to unnecessary or excessive purchases and through expiration of a product's shelf life.

- Segregate waste streams to allow for certain wastes to be recycled or reused and to keep non-hazardous materials from becoming contaminated.

- Improve material handling procedures such as using a minimum of non-hazardous materials (e.g., absorbent, water) to clean up hazardous material spills.

- Prevent and contain spills and leaks by installing drip trays and splash guards around processing equipment.

- Ensure that product and waste containers are kept closed except when material is added or withdrawn.

- Track wastes and include careful labeling to ensure safe handling of wastes, and identification of wastes which have the potential for recycling or resale.

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Technology Modifications

Some products can be manufactured by two or more distinct processes, and one process may produce less hazardous waste than the other. Technological modifications can be generally categorized as:

Technology Modifications

- Process modifications which may reduce raw material consumption, increase production, and improve product quality as well as reducing waste,
- Equipment modifications, which can reduce or eliminate equipment-related inefficiency,
- Process automation, including use of automatic or mechanical production devices or installation of computerized process monitoring and adjustment systems, which may result in the generation of less waste, the use of less energy and raw materials, and the production of a higher quality or quantity of product,
- Changes in operation settings so optimum performance is achieved,
- Water conservation which reduces the volume of wastewater requiring treatment or disposal, and minimizes your water bill, and
- Energy conservation which minimizes wastes such as those associated with water treatment, cooling water blowdown, and boiler blowdown.

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Extend The Life Of Process Solutions

- Replenishment of baths; by adding necessary chemicals bath life may be increased.
- Use purer anodes, or regenerate plating solution through filtration.
- Reduce drag-in by better or modified rinsing.
- Cover baths with lids when not in use. This will reduce product losses through evaporation.
- Test process bath for pH, metals and other indicator parameters to determine when additional chemicals should be added or when metal contaminants should be removed.
- Properly design and maintain racks to reduce build-up of corrosion and salt deposits which will contaminate plating solution.

Extend The life of Your Processing Solutions

The lifetime of a plating solution is limited by the accumulation of impurities and by depletion of constituents due to drag-out. The build-up of impurities can be limited by the following techniques:

Dragout Reduction

Plating solution which is wasted by being carried over into the rinse-water as a processed part is moved from the processing solution into the rinse is defined as "drag-out", and is the largest volume source of pollution. Numerous techniques have been developed to control drag-out. The efficacy of any technique will function with the geometry of the parts processed, operator technique used, racking methods, plating barrel design/loading, transfer times, dwell times, and numerous other variables.

Reducing the dragout reduces the amount of rinse water needed. Also, less of the plating solution metals leave the process, which ultimately produces savings in raw materials, treatment and disposal costs. Dragout reduction techniques include the following:

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Reduce Solution Drag-Out

Lower the concentration of plating bath constituents. This will save material cost, reduce solution viscosity and dragout, and reduce the toxicity of bath solutions generated.

Increase plating solution temperature to reduce both viscosity and surface tension of the solution.

Use nonionic wetting agents to reduce solution surface tension.

Withdraw work-pieces at a slower rate to allow maximum drainage back into process tanks.

Install drainage boards between tanks to route dragout into the correct process tank.

Properly design and maintain rack systems. Properly place work-piece on the rack to reduce dragout.

Train personnel or program automatic machinery to allow for optimum drain times

Install drain bars on hand operated lines to allow workers to momentarily rest the parts and drain them before moving to the next process. This normally does not affect productivity significantly.

Install fog sprays or air knives on hot process tanks that can accept the added liquid volume.

Rack parts for optimum drainage

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Reduce Water Usage

- Install automatic flow controls.
- Install multiple rinse tanks in a countercurrent series system.
- Use sprays or mist to rinse off excess process solutions.
- Agitate the rinsing-bath mechanically or with air to increase rinsing efficiency.

Reduce Rinse Water

Rinse water reduction involves rinsing the work-piece in the most efficient manner, thereby using the smallest volume of rinse water possible and in turn reducing treatment needs, sludge generation, and ultimately saving money.

Recycling

Recycling is the use, reuse, or reclamation of a waste after it is generated by a particular process. Examples of recycling opportunities include:

Recycling Process Solutions

- Install rinse water treatment systems which recover process solutions and allow recycling of the rinsewater.
- Use spent acid/alkaline solutions to adjust the pH of the treatment system.
- Return spent plating solution to the manufacturer, whenever possible.
- Recover plating metals from sludge.

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Treatment Alternatives

Finally, in some cases alternative treatment methods can reduce the toxicity or volume of certain waste streams which cannot be eliminated.
For example:

Treatment Alternatives

- Use treatment technologies which do not generate heavy metal sludges such as ion exchange, evaporation, or electrolytic metal recovery.

- Use different precipitating agents which generate less sludge, such as caustic soda instead of lime.

Reduction Of Waste Generation
We can reduce wastes generated by utilizing one or more of the following:

Reduction Of Waste Generation

CHEMICAL SUBSTITUTION
WASTE SEGREGATION
PROCESS MODIFICATION
RECYCLE/REUSE

We shall define these and go into details shortly. But first, a word of caution:

Too often, advice is given or taken without complete understanding of the FULL ramifications of a given waste minimization decision. At least one major captive plater installed evaporative recovery with full intention of returning the concentrated brass plating solution to the plating tank. Within one year after the installation was complete, however, this same plater resorted to hauling the concentrate away rather than deal with the rejects caused by the buildup of impurities. Is waste minimization practiced when the waste is simply concentrated? The answer is NO.

There also is a significant amount of misinformation available as to what steps will result in reduced waste. A case in point is a text on Waste Minimization that offers this advice: "The plant currently treats chromium waste with sodium bisulfite to reduce chromium,

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this requires the pH of the waste to be between 2 and 3. The acid used to lower the pH and the caustic used to raise the pH will contribute to sludge volume. The company should consider reduction with ferrous sulfide (typo. I think the author meant sulfate) which doesn't require pH adjustment to 2." This is of course, totally erroneous and the typo makes the information presented dangerous to boot! Ferrous sulfate generates four times as much sludge as bisulfite in chromium reduction and clarification.

Another example of possibly bad advice:
" Plant A should consider replacing its cyanide process chemistries with chemistries that do not contain cyanide." Unfortunately, the processes referred to in plant A are Copper, Cadmium, and Silver plating. Non cyanide copper plating is only in pilot plant stage, non cyanide silver plating is available from only one supplier and is troublesome to operate, and non cyanide cadmium plating can be non productive on heat treated parts. The point to all this is that you can make intelligent decisions on waste minimization only after you have obtained full knowledge about your process and the requirements placed on your product. You must also have knowledge about how metal finishing principles can affect waste generation. Nothing we present here will work in all cases and at all times. This chapter intends to provide enough information (including potential problems) to guide you in the direction of waste minimization. The final decision and responsibility will belong to each individual facility.

How Basic Metal Finishing Principles Can Affect The Amount Of Waste Generated

SOLUTION CHEMISTRY

A typical plating bath contains a compound that yields the metal ions for plating plus other ingredients for:

Solution Chemistry

Conductivity
Anode Corrosion
pH Stabilization
Impurity Complexing
Brightening
Levelling Etc.

Solution chemistry can influence waste generation when the chemistry forms insolubles during waste treatment. Ingredients that often form insolubles in waste treatment are:

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Ingredients That Form Sludge

Sulfates
Phosphates
Silicates
Sulfides
Carbonates
Iron Compounds

By avoiding any of these ingredients in your processing chemistries or by reducing the concentration of the compounds containing these ingredients, the quantity of waste generated can be reduced. Of course, there are times when one or more of the above chemicals is purposely added at the point of waste treatment to improve performance.

In such cases, be sure to add as little as is absolutely necessary and be sure the chemical is truly needed. We recently visited a plant adding carbamates (organic sulfides) to improve copper removal in their clarifier. When we tested their raw waste, we found their dissolved copper was already far below regulated levels. The CLARIFIER was not doing its job. Carbamates won't help in such cases.

REACTIONS AT THE CATHODE
At the cathode, we have two competing reactions:

Reaction At The Cathode

1. Metal Ions Are Converted To Solid Metal

2. Hydrogen Ions are Converted To Gas

Gas Evolution Reduces Solution Efficiency and Creates Air Pollution

Reduce Hydrogen Evolvement By Maximizing Agitation, Temperature, Process Chemistry

1. Metal ions are being reduced to solid metal by combining with electrons supplied by the rectifier.

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2. Hydrogen ions are similarly reduced by "competing" with the metal ions for the available electrons.
As a result of these competing reactions, in most plating chemistries, some hydrogen is evolved. This results in the discharge of hydrogen gas. The quantity of metal plated vs the amount of gas discharged is known as the process "efficiency". Processes with low efficiency generate a lot of gas and often require ventilation and scrubbing systems. Scrubbing systems generate waste unless specifically designed to utilize recycling. The efficiency of most plating processes can be maximized by use of good agitation (avoid air agitation if possible), good pH control where applicable, frequent analytical control of the chemistry, and operating at the upper end of the allowable temperature range.

REACTIONS AT THE ANODE
At the anode, we also have competing reactions:

Reactions At The Anode

1. Solid metal is converted to ions with help from the rectifier.

2. Hydroxide ions are converted to oxygen with help from the rectifier.

Reaction 2, Creates Anode Sludge/Waste

Improve Anode Efficiency By:
- Keeping hooks clean
- Maintaining Correct Anode Surface Area
- Good Agitation
- Good Temperature Control
- Use Correct Anode For The Process

If reaction 2 is allowed to proceed, the anodes become passive and the oxide film that forms on their surface must be cleaned off...usually with strong acid pickles. Such cleaning operations generate a significant amount of waste. Anode passivity can also result in more solids being introduced into the plating solution (less filter life). Anode efficiency can be improved by following the guide in the slide.

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Drag-Out Volume Depends On:

Solution Viscosity
Part Geometry
Drain Time
Surface Tension
Metal Concentration In The Process

DRAG-OUT

Much waste minimization effort goes into reducing drag-out. The amount of waste generated by dragout depends on a number of factors:

The last variable is a result of another metal finishing principle. When confronted with the task of reducing waste generation, there is a temptation to reduce "Drag-Out" by reducing the concentration of the process bath. This can be good or bad advice.

The plating principle at work here is an equation called the "Nernst Equation":

$$E = \frac{E^\circ + 0.059 \log C}{n}$$

Where E is the theoretical plating voltage, E° is the standard electrode potential, and C is the concentration of the metal ion. The more positive the value of E, the more readily the metal deposits (plates). If we reduce the concentration of the metal ions (for example, if we decided to plate with 22 oz/gal of chromic acid instead of 33), then E becomes more negative and our efficiency drops dramatically. Small reductions in metal ion concentration, however, can be successful if we keep in mind the impact on efficiency and make appropriate adjustments such as decreasing current density, increasing agitation and increasing the temperature.

Good agitation decreases the thickness of the cathode film where plating occurs. It also increases the current density at which we can plate. The most popular method of agitating is to use low pressure compressed air. While it is the most popular, this method of agitation is the least effective and produces waste due to the necessity of scrubbing the exhausted air. You can also get into OSHA trouble by air agitating concentrated rinse tanks (such as the first tank in a counterflow rinse) which do not normally have ventilation hoods!

INCREASING TEMPERATURE

We've also mentioned increasing the temperature several times. What does this do for us?

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Increasing The Operating Temperature
Benefits:

Increases Ionic Activity
Increases Ion Diffusion Rates

The effect of increased ion activity and diffusion rates is to counteract the negative effects of reduced ion concentration.

Drawbacks:

Increased Brightener Consumption
Increased Cyanide Breakdown/Carbonate Buildup
Tank Lining Attack
Increased Energy Costs

By increasing process temperatures you will also get another side benefit....increased evaporation. If you can increase the operating temperature you will have more room in the process bath for you to return the plating solution from a dragout tank.
The drawbacks to increasing temperature include those shown on the slide.

How Should You Start Your Pollution Prevention Program?
A plant assessment is your first step. Analysis of operations can identify the plant changes that will reduce chemical loss and water use. Resulting savings usually quickly re-pay costs involved in implementing the program.

Typical steps involved in a plant assessment for pollution prevention purposes are:

1. Locate (or prepare, if necessary) plans or drawings of the layout of the metal finishing area. These drawings should be to scale, identifying and showing the location of all relevant equipment and tanks. Plating lines should be identified. Gutters, sumps and sewer lines should be indicated. Water lines, control valves and flow regulators should be identified.

2. With this information, you can now review and document all operations of the plating room that relate to chemical or water use. Be sure to examine each plating line, as there may be differences in sequence or plating requirements. The next slide shows examples of the types of information you will be documenting.

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Starting Your PP Program:

1. Locate/prepare drawings/layout of facility

2. Review/document all operations where chemicals/water are used:

   Estimates of production (i.e. square meters plated; number of parts, barrels of racks to pass through a process line.

   Purchases of chemicals and break-down of where each chemical is used, how much...
   Rinsing and draining times on automatic lines

   Efficiency of operators in rinsing and draining on manual lines

   Relative amount of dripping onto the floor, if applicable.

3. Now, you can examine process water use. Review past water bills to determine expected water use, per day or minute. Measure and record water use at each process step. Especially watch rinse flow rates, as this is where most water is used. (Water meters on each line would be extremely useful). With these two sets of information, do a water balance. A difference of 15 % or less is generally acceptable. If the variance is larger, you should determine the reason. Here are some possible causes of such differences:

wash-downs;- unattended running hoses; - non-rinsing uses of water, such as fume scrubbers, heat exchangers, boilers, etc.

4. Your assessment will also include sampling and analysis to determine the nature and characteristics of waste streams. Of course, the final effluent will be analyzed to determine which pollutants are not in compliance with requirements. As part of the assessment, you will also sample all individual rinse tanks, overflows, batch dumps, and plating solutions (to allow calculations of drag-out).
These additional samples are used to isolate sources of pollution, to calculate chemical losses, and to evaluate potential benefits of drag-out reduction and flow minimization techniques.

5. You will also want to evaluate drag-out. Drag-out measurements are performed at

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Starting Your PP Program

3. Examine Process Water Use
   - Water Bills
   - Measure Each Use
   - Balance (15% match desired)

4. Sampling and Analysis
   - Rinses
   - Spillage
   - Drippage
   - Drag-out

5. Quantify Drag-ou

6. Information On Spent Solutions
   - Cleaners
   - Acids
   - Chromates
   - Strippers

7. Analyze the Data

plating tanks to determine the pollutants contributed by these sources. This information is used to evaluate the applicability and potential benefits of changes made to minimize drag-out, and changes made to the rinsing systems.

6. You will collect information about batch dumps that result form the process. Batch dumps can contribute significantly to effluent concentrations of pollutants, as well as cause significant pH fluctuations in the plant wastewater stream. To obtain further information about what happens in your operation, you might consider developing a dump schedule and a simple materials balance for an individual department or processing area. In a materials balance, you try to account for all materials that enter and leave a processing area. This can help you improve process control, and improve other operational aspects such as cleanup procedures.

7. Finally, use all this information to analyze the entire plating operation. Your objectives are the elimination, recovery or reduction of wasted chemicals and wasted water. Accomplishing these objectives will save you money, and at the same time reduce or eliminate pollutant discharges from your plant.

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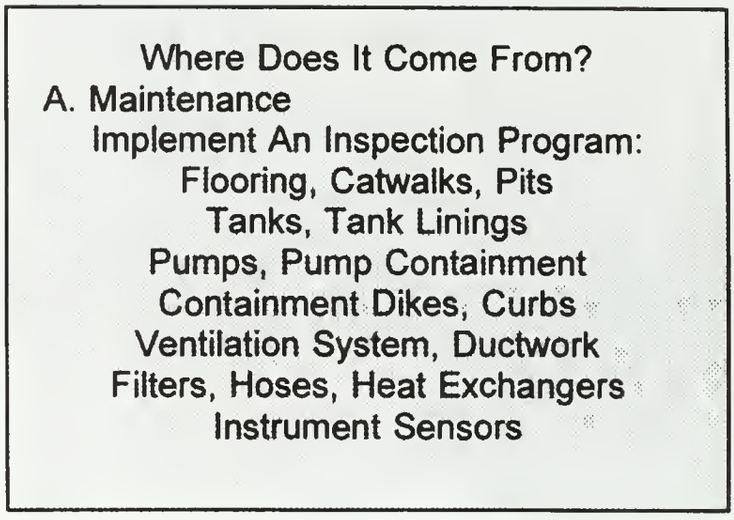

WHERE DOES IT COME FROM?

We can go a long way towards minimizing (and sometimes eliminating) waste, if we can itemize the origin(s) of this adversary. So let's begin this section on Waste Minimization by discussing the sources a metal finishing shop has available for the generation of waste. Once this list of sources is refined for your individual plant, the next steps; waste reduction, substitution, recycling, and process modification may become "self evident" Typical metal finishing processes and the wastes they generate are on the next page (A more complete list of chemicals typically used in metal finishing is provided at the end of this chapter).

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Typical Metal Finishing Processes and Wastes They Generate

Process	Heavy Metals	Cr^{+6}	CN	FOG	SOLIDS	AIR EM.
Acid Pickling	X	X			X	X
Alkaline Cleaning	X		X	X	X	
Anodizing	X	X		X	X	X
Bright Dips	X				X	X
Chromating	X	X			X	X
Deburring	X			X	X	X
Degreasing				X	X	X
Electrocleaning	X		X	X	X	X
Electroless Plating	X				X	X
Passivating	X	X			X	X
Phosphating	X	X		X	X	X
Polishing/Buffing	X			X	X	X

Where Does It Come From?

Poor Maintenance

Inspect flooring
Inspect all tanks/linings
Inspect all pumps
Keep spare parts
Inspect containment systems
Inspect the ventilation system
Inspect all filter hoses and connections
Inspect heat exchangers, steam traps, and instrument sensors.

Maintenance

There are metal finishing plants where maintenance personnel seldom spend any time on the plating equipment and infrastructure, and if they do, it is only because an emergency has arisen. Maintenance personnel must be responsible for inspecting on a routine basis

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(weekly preferred) the infrastructure of the facility:

. Inspect flooring and repair any cracks subject to wetting by chemicals immediately . Inspect joints and repair immediately if damage is detected.

. Inspect all tanks, tank linings for deterioration. Make immediate repairs on repairs on tanks identified as "critical". If damage is detected, always inspect the adjacent tank too.

. Inspect all pumps, focusing on seals and repair those identified as "critical" immediately. Keep spare parts.

. Inspect containment dikes and other containment systems for signs of leakage. Make repairs as soon as damage is found.

. Inspect the ventilation system for signs of damage to ducts, scrubbers, packed towers, fans, fan belts, hoods.

. Inspect all filter hoses and connections.

. Inspect all heat exchangers, steam traps, and instrument sensors.

In some plants, it is still part of the routine, to hose down the outside of all tanks and the superstructure with a high pressure water hose. This results in the generation of many gallons of dilute waste that requires treatment and adds to the already accelerated corrosion faced by all materials of construction in the facility. Maintenance personnel should be trained to replace "hose downs" with "sponge-ups". At times, the sponged up chemicals can be returned to the process tank. Even when this is not possible, smaller volumes of concentrated clean up solution from segregated areas can be used for pH adjustment. Another solution is to design the facility so that the exterior of the tanks stay as clean as possible (drip pans, automated hoists, manual hoist systems), or to make the tanks out of material that will allow the accumulated chemicals to remain without trouble. You can also reduce waste from chemical spills by:

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Reduce Waste From Chemical Spills By:

Preventing the loss of chemicals to the environment as a result of leaks, accidents and deliberate dumps.

Provide curbing around plating bath filters.

Route condensate from exchangers and coils in cyanide solutions separately.

Use drain boards to prevent spillage between process tanks.

Prevent overflows from the "topping up" of process tanks.

Remove all valves from the bottoms of process tanks and rinse tanks that contain concentrated rinsewater.

Inspect all tanks with bottom flanges and valves on a scheduled basis.

Make chemical additions easy to do.

Prevent the loss of chemicals to the environment as a result of leaks, accidents and deliberate dumps. Possible sources of accidental losses include tank leaks, equipment leaks, spillage between process tanks, overflows, accidental opening or rupture of a valve; and the spilling of chemicals in storage or during application.

Provide curbing around plating bath filters to recover leakage that is inevitable when servicing/changing media.

Routing condensate from exchangers and coils in cyanide streams separate and directed to the cyanide treatment system. Similarly, condensate from exchangers and coils in chromium streams should be separately directed to the chrome treatment system. This prevents the possibility of a toxic chromium-cyanide reaction.

Use drain boards to prevent spillage between process tanks. A drain board could be a plastic coated drain tray, piping, or tank lining continued from one tank to the next.

Prevent overflows from the "topping up" of process tanks, by using spring loaded nozzles, separate water lines, or float level controllers, if water is added directly from

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piping.

Remove all valves from the bottoms of process tanks and rinse tanks that contain concentrated rinsewater. Seal the flanges at the bottom of tanks permanently.

Inspect all tanks with bottom flanges and valves on a scheduled basis (preferably monthly).

Make chemical additions easy to do. Add only small amounts at any given time. Purchase liquid concentrates instead of solids whenever economical (sometimes even when it costs more). This is especially true with cleaners. However, acids should be replaced with acid salts, if possible, due to the hazardous nature of liquid acids. Instruct operators to dissolve all chemicals before they are added to process tanks.

Waste Generated by Corrosion:

Inspect metal tanks for stray currents and correct ASAP.

Avoid the temptation to line the inside and the outside of steel tanks because it makes pinholes almost impossible to detect (until the tank collapses).

Construct tanks of corrosion resistant materials such as polypropylene, fiberglass, Kynar, stainless steel, and composites.

Protect all bare concrete surfaces subject to chemical spills/splashes with sealing materials.

Corrosion

A significant amount of waste is generated either by combating or surrendering to corrosion. Consider implementing an inspection program to protect against corrosion and design corrosion resistance into your plant:

Pilot Studies

Avoid Accepting "free" Samples

Treat Waste From Pilot Studies Separately or Return to Vendor

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Pilot Studies
That experimental line or testing bench tucked away in the bosom of your plating department probably has accumulated many pounds of chemicals and chemical products that were obtained "free" from suppliers or other shops (as they went out of business!). Unfortunately, after such largess is accumulated, you usually find that much of it is useless and must be disposed of. Your options are:

. "Lab-packs", cost of approximately $1000.00/drum.

. Bleed into your waste treatment system.

Neither option is highly desirable. The first is expensive while the second contributes to a higher generation of hazardous waste. For example, each gallon of nickel plating solution waste treated generates about 3.5 gallons of 2% solids sludge. Organic chemicals are potential disasters. They are normally not compatible with waste treatment systems and their presence is often cited for rejecting a waste from a disposal facility. Be sure to check any organic containing product against the accompanying MSDS for the presence of regulated/banned substances. When you find such chemicals, attempt to locate a substitute that is not heavily regulated. If this is not possible, purchase only the amounts you are sure to consume in a reasonable time frame.

Metal finishing laboratory discharges should be routed through the waste treatment system, not directly to the sewer.

Inert Anodes
Because most plating baths work faster and with fewer contamination problems, when the metal content is kept on the high side of the recommended operating range, plating personnel naturally favor high metal concentrations. If you have a recovery system on a plating process, it also will tend to increase the metal concentration of the plating solution. This tends to be counterproductive, in that the higher the metal concentration, the more metal is dragged out of the process tank and the more metal ends up in the treatment system (resulting in more waste).

The answer is to use inert anodes wherever possible to compensate for the metal returned by the recovery system. Try to operate the plating bath at the LOW end of the acceptable concentration range. The benefits are:

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Using Inert Anodes

Less Drag-out....Less waste
Less waste from the scrubber
Smaller recovery system required
Less rinse water required
Lower fugitive emissions

On the negative side:

More frequent analysis
More sensitivity to contamination
Depending on the process, you may see a slower plating speed.

Hand Line Operators

Install Pulleys and Hoists To Reduce Floor Drips

Train Operators To Hold Parts 15-20 Seconds For Draining

Train Operators To remove Dropped Parts From Tanks ASAP

Train Operators To Properly Maintain Racks

Hand Line Operators

A lot of waste is generated when tank personnel remove racks of processed parts and splash chemicals all over the floor. Often, this is not the fault of the personnel. Many plating companies utilize racks that are oversized and unwieldy for one person to handle. We have seen pulley systems installed over hand line tanks. These allow the operator to easily hold the part over the tank for 15-20 seconds, allowing the process solution to drain back to the tank. The rack can then be hand carried to the rinse tank. A manual or automated hoist is, of course, the ultimate answer, but is often too expensive, or can not

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be implemented in older shops with tank sequences that look like jig-saw puzzles.

Hand-line operators are also notorious for dropping parts into the process tanks and leaving them there to form "sludge" which may not be removed until the annual shut-down and clean-up of the tank. This also may not necessarily be the total fault of the operators. Racks are often poorly maintained, contacts are heavily plated, preventing a firm grip on the parts. There is no excuse, however, for not removing dropped parts from tanks.

Hand Operated Barrel Lines

The above discussion for hand line operators, takes on a whole new meaning when considered for hand operated barrel plating lines.

Here are approaches you should consider to reduce drag-out from barrel plating lines:

Reducing Waste From Barrel Lines

Slow Withdrawal

Rotate Barrel If Parts Are Complex/Cup Shaped

Tilt Barrel To One Side To Help Drainage

Use Barrels With Largest Holes

Maintain Barrel Holes/Doors

Use Designated Barrels, Whenever Possible

. Generally, slow withdrawal and draining over the plating tank reduces the volume of drag-out by allowing more time for drainage back into the tank.

. The shape of the parts being plated will have an effect on barrel drag-out. For simple parts which do not collect or hold solution, it is probably best that the barrel not be rotated during withdrawal. On the other hand, if pieces will tend to hold solution, barrels should be rotated during withdrawal and drainage. (You could test a load with, and without rotation to decide the best approach.)

. Use plating barrels with the largest holes possible. Newer designs with laser drilled, tapered holes and with holes on the ends as well as the walls drain

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faster. Maintain the holes by drilling out accumulated fines that plug small holes. Also maintain the doors, so small parts such as fasteners don't fall out and end up as "sludge" at the bottom of the plating tank.

. Consider using "designated" barrels for cleaning and acid dripping prior to plating. The danglers won't get plated, resulting in lower metal contamination of the cleaners and acid. This increases the life of the cleaners/acids, reduces maintenance and "down time" of the barrels prior to plating, the rinsewater after cleaning/acid dipping can often be discharged directly to sewer (sometimes pH adjustment is needed). The disadvantage is the added labor of unloading and re-loading the barrels midway through the cycle.

Reducing Waste From Filters

Locate Inside Tank, Whenever Possible

Filters Outside Tank Should Be Contained

Connect To Tank Permanently, If Possible
(Avoid Hoses/Tubing)

Use Filters With Re-usable Media

Filters

Filters are a big potential source of waste. If your process filters are located outside the process tank and are the type that require pre-coating or cartridge changes, you are probably generating avoidable waste. Filters should be placed inside the process tanks if possible. If they can not be placed inside the process tanks, they should be inside containment trays, so that spillage that normally occurs during service, and leakage from pumps/seals is collected for re-use or channeling to waste treatment. Some newer filter designs incorporate elements that can be manually cleaned and re-used, eliminating the need to dispose of spent cartridges, pads, and disks. Pumps should be located high enough to prevent siphoning of process solution from the tank in event of malfunction.

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Reducing Waste From Spent Solutions

Use Liquid Cleaner Concentrates Instead Of Powders

Use Weak Acids Or Acid Salts

Extend Chromate Life Through Chemical Control

Keep Acids At Low End Of Operating Temperature

Spent Solutions

Studies at various metal finishing facilities have shown that as much sludge is generated from the cleaners, acids, and chromates and their associated rinses as is generated from the plating rinses. Cleaners and acids become contaminated with heavy metals from the danglers in plating barrels or from metal build-up on rack tips. Cleaners have a tendency to accumulate solids at the bottom of the tank, from dropped parts and from additions of powdered or granulated solid cleaner. One plater discovered his cleaners lasted three times longer and were significantly more effective after he switched to a supplier of liquid concentrate cleaners. The diluted concnetrate eliminated the need to dissolve solids, saving labor as well. Acids should be kept as weak as possible to avoid unnecessary attack of basis metal. Inhibitors are helpful as long as they do not contaminate the plating solution. Chromate life can be extended by careful control of pH, keeping immersion times as short as possible, and employing temperature control (keeping it at the low end of the acceptable temperature range).

Waste From Ventilation Systems

Increase Freeboard On Ventilated Tanks

Use Correct Capture Velocity

Use Foam Blankets/Poly Balls

Recycle Scrubbing Water, If Possible

Use Updraft Ventilation, If Possible

Ventilation Systems

Your ventilation system can add to your waste generation in several ways. Scrubbers,

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de-misters, and condensate traps yield concentrated wastes that require treatment unle exhaust streams are segregated and collection/purification systems are employed. Process solutions that generate mist (chromium plating baths, air agitated nickel/copper baths etc.) should be in tanks with more freeboard. These processes should also employ foam blankets, floating polypropylene balls, and updraft ventilation. Updraft ventilation. Updraft ventilation allows mist to "condense" in the duct-work and flow back to the process tank. Using the correct capture velocity is important. Too little ventilation air is a safety and corrosion hazard, while too much creates excessive emissions and reduces scrubber efficiency.

Reducing Waste From Vapor Degreasers

Keep High Freeboard

Use Refrigeration

Replace Old Degreasers

Add Cooling Coils

Train Operators At Slow Withdrawal

Locate Degreasers Away From Drafts

Vapor Degreasers

When toxic chemical release reports were first required, one plater was very surprised to discover that he discharged over 60,000 lb of trichloroethylene (into the atmosphere) annually! Frankly, this is very easy to do. The amount of solvent discharged into the atmosphere can be affected by such diverse variables as freeboard, use of a lid, ventilation rate, operating temperature, level of cooling/refrigeration, work withdrawal rate, solvent density, and solvent stability. In one plant, the degreasers are located in the vicinity of large overhead doors which the operators frequently leave open (to improve the climate inside the shop). The uncontrolled drafts caused by the doors literally vacuum the solvent out of the degreaser and work counter to the ventilation system. The net result is significant loss of solvent and an unhealthy working environment.

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CHEMICAL SUBSTITUTION

When pursuing a program of pollution prevention, the second alternative after elimination is substitution. If we can substitute a process that generates less waste that the one currently in use, we will be contributing to the prevention of pollution. Since there is no "free lunch", we will be paying a price for this act and we need to know as much as possible about the substitute process to make an intelligent decision so that the price will not be too dear. The following are features of popularly touted substitutes for existing coatings or chemical processes in metal finishing shops.

The incentive for substituting process chemicals containing non-polluting materials has only been present in recent years with the advent of pollution control regulations. Chemical manufacturers are gradually introducing such substitutes. By eliminating polluting process materials such as hexavalent chromium and cyanide-bearing cleaners, and deoxidizers, the treatments required to detoxify these wastes are also eliminated. It is particularly desirable to eliminate processes employing hexavalent chromium and cyanide, since special equipment is needed to detoxify both.

Substituting non-polluting cleaners for cyanide cleaners can avoid cyanide treatment entirely. For a 2 gal/min rinsewater flow, this means a savings of about $12,000 in equipment costs and $3.00/lb of cyanide treatment chemical costs In this case, treatment chemical costs are about four times the cost of the sodium cyanide cleaner.

There can be disadvantages in using non-polluting chemicals. Before making a decision, the following questions should be asked of the chemical supplier:

Substitution; Questions To Ask:

Are substitutes available and practical?

Will substitution solve one problem but create another?

Will tighter chemical controls be required of the bath?

Will the change involve any cost increases or decreases?

Who Else Is Using This Process Successfully?

How Long Has This Process Been On The Market?

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Some commonly recommended chemical substitutes are:

Some Commonly Recommended Substitute Processes:

POLLUTING	SUBSTITUTE	COMMENTS
Heavy Copper Cyanide Plating Bath	Copper Sulfate	Excellent throwing power with a bright, smooth, rapid finish. A copper cyanide strike may still be necessary for steel, zinc, or tin-lead base metals. Requires good pre-plate cleaning. Non-cyanide process eliminates carbonate build-up in tanks.
Chromic Acid Pickles, Deoxidizers, & Bright Dips	Sulfuric Acid and Hydrogen Peroxide	Chromium-free substitute. Non Fuming.
Chrome Based Anti-Tarnish	Benzotriazole (0.1-1.0% solution in methanol) or water-based proprietaries	Chromium-free substitute. Extremely reactive, requires ventilation.
Cyanide Cleaner	Tri-sodium-Phosphate And Proprietary Cleaners	Cyanide-free cleaner. Good degreasing when hot and in an ultrasonic bath. Highly basic. May cause wastewater treatment problems.

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Chemical suppliers can also identify any regulated pollutants in the facility's treatment chemicals and offer available substitutes. The federally regulated pollutants are cyanide, chromium, copper, nickel, zinc, lead, cadmium, and silver. Local and/or state authorities may regulate other substances, such as tin, ammonia, and phosphate.

Other Substitutes for Popular Metal Finishing Processes:

Trivalent for Hexavalent Chromium

Regulations under the Clean Air Act, along with local constraints on chromium emissions to the air and water, plus the "stigma" hexavalent chromium has obtained as a health hazard are the driving forces behind the push for substitution of hexavalent chromium plating processes with baths made from trivalent chemistries. While the trivalent process has produced "hard" chromium deposits exceeding .0005" in the research laboratory, at the present time, there is no commercially viable hard chromium plating process using the trivalent chemistry.

PROCESS DIFFERENCES:

Cr^{+3}	Cr^{+6}
Filtration	No
Air Agitation	No
Carbon Treatment	No
Heat/Cool	Yes
No Vent	Vent
No Scrub	Scrub
Less Energy	More
Proprietary Anodes (Cl)	No
Membrane Cells (SO_4)	No
Lead Anodes (SO_4)	Yes
Burn Proof	No
Current Interrupt OK	Not OK
Analysis Important	Not As Much
pH Important	No
3-5 cents/ft^2	2-3 cents/ft^2
Corrosive Solution	No

Process Differences

The trivalent chromium plating process has been available to the plating industry since 1973. The chloride based chemistry came first and was followed by the sulfate based process. The process requires filtration, air agitation, carbon treatment, and heating. The chloride based process requires cooling in addition to heating. The hexavalent process functions very well without any of these, except for heating/cooling. The trivalent processes operate within OSHA standards without direct ventilation, while the hexavalent

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bath must have an installed exhaust/scrubber system. The trivalent baths use less energy overall because no make up air is heated to compensate for loss through ventilation. The trivalent baths do not need air permits and OSHA headaches are reduced.
The chloride based process utilizes proprietary graphite anodes that are designed to prevent the formation of hexavalent chromium. These anodes disintegrate over time and must then be replaced. The sulfate process utilizes lead or lead alloy anodes that are encased in a cell. The cell has a membrane walls that allow transfer of electricity and certain ions, but reject trivalent chromium, thereby preventing the formation of hexavalent chromium at the anode.
The cell contains approximately 10% sulfuric acid which periodically (every 3-6 months) requires changing and waste treatment (there will be some heavy metals in the acid, including lead). The cell membranes have a finite life and are expensive to replace. They also require careful handling to avoid damage and leaks.

One of the more unique features of the trivalent baths is that they are almost "burn" proof. That is no matter how high the current density is, the deposit will not turn powdery/grey. The throwing power of the trivalent process is exceptional, yielding coverage around recesses and drilled holes that is far better than with hexavalent baths.

Trivalent baths tolerate current interruptions, while hexavalent baths produce dull white deposits if the current goes off during the plating cycle. Trivalent baths can not tolerate heavy metal contamination to the same degree as hexavalent baths. While hexavalent baths can produce a beautiful decorative deposit while containing many thousands of parts per million of heavy metal contaminants, trivalent baths are detrimentally affected by several hundred parts per million of heavy metal impurities. Trivalent baths require routine purification and carbon treatment, while hexavalent baths do not.

Analytical control of trivalent baths is more critical because these baths contain very low concentrations of chromium (as little as 0.7 oz/gal vs 33 oz/gal for hexavalent baths). In addition to bath chemistry, the pH of the trivalent baths must be monitored and controlled while pH is not of concern in hexavalent baths.

After factoring chemical, analytical, waste treatment, waste disposal, and energy costs, trivalent baths are slightly more expensive than hexavalent. Reported costs for trivalent baths range 3-5 cents per square foot while hexavalent costs range 2-3 cents per square foot.
Hexavalent baths do not promote corrosion, if the plating solution is not adequately rinsed from crevices, while the trivalent processes can seriously deteriorate steel surfaces if allowed to remain (especially chloride). This can be compensated through he use of a "post treatment" following plating. Some of these post treatments contain hexavalent chromium, thereby negating some of the benefits of substituting trivalent for hexavalent.

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DEPOSIT DIFFERENCES:	
Cr^{+3}	Cr^{+6}
Darker	Pleasing Light Blue
Poorer Corr. Res.	Better
Good Wear Res.	Same
No Thick Deposits	Thick Deposits

Deposit Differences

The trivalent processes tend to produce a deposit that is generally considered to be darker in appearance that the hexavalent processes and baths that are carefully controlled to yield an appearance that is extremely close to hexavalent deposits are inconsistent. If impurities are not kept at a very low level, color matching of parts plated months apart can become a difficult proposition. Trivalent baths produce a deposit that is micro-porous. This enhances the corrosion resistance of the plated coatings when applied over nickel plating that is greater than 0.00025" in thickness. When the nickel thickness is less than 0.00025", the trivalent chromium provides less corrosion resistance than a "crack-free" deposit from hexavalent baths because there is inadequate nickel to delay the on-set of base metal corrosion through the normal distribution of the corroding current over a larger area. Trivalent deposits in excess of 0.0005" tend to be stressed and have very low corrosion resistance due to excessive porosity.

The wear resistance (hardness) of a trivalent chromium deposit is similar to that of a hexavalent deposit. Stripping trivalent deposits with hydrochloric acid is difficult and slow. Reverse current stripping is usually employed. This "resistance" to hydrochloric will also affect the ability to measure the thickness using chemical stripping methods such as the hydrochloric spot test.

POLLUTION PREVENTION POTENTIAL:	
Cr^{+3}	Cr^{+6}
5-10% As Much Sludge	More
No Reduction	Reduction
Higher COD	No COD
Recovery Possible	Possible

Pollution Prevention

Trivalent chromium chemistries can be expected to generate between 5 and 10% as much solid waste from waste treatment of rinsewater, due to lower chromium content in the drag-out, when compared to hexavalent baths (assuming no recovery of drag-out). Trivalent baths require no reduction step, only pH adjustment. This translates to lower capital costs for waste treatment, and no "hexavalent" violations due to malfunctions of the reduction system. For companies that must comply with COD (chemical oxygen

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demand) regulations, trivalent baths will increase your COD loading because they contain a significant amount of organic additives. No exhaust from the process means no air permit, no scrubbing equipment, and no treatment/disposal of scrubbing media. Suitable recovery methods are available for both hexavalent and trivalent chemistries.

WORKER SAFETY/ECONOMICS:	
Cr^{+3}	Cr^{+6}
Not Carcinogen	Carcinogen
0.5 mg/M^3	0.05 mg/M^3
No Fire Hazard	Fire Hazard
Not Skin Corrosive	Skin Corrosive
More Expensive	Less Expensive
Color Problem	Color No Problem

Worker Safety/Economic Issues

Hexavalent chromium is listed as a suspected carcinogen, trivalent, at this time, is not. OSHA regulates hexavalent chromium at 0.05 mg/cubic meter while trivalent chromium is regulated at 0.5 mg/cubic meter.

Hexavalent chromium plating solutions and chemicals are fire/explosion hazards while trivalent baths are not associated with such hazards.

At the present time, a metal finisher outside the USA with a hexavalent chromium plating process can successfully compete with a plater using the trivalent process on the basis of economics and esthetics. A significant number of chromium platers in California have substituted trivalent chromium for hexavalent baths. One plater operates both baths, and reports that the hexavalent process consistently outperforms the trivalent process in appearance. Another plater performing trivalent chromium plating only, dares anyone to tells the difference.

Alkaline Non Cyanide Copper for Cyanide Copper

Since 1990, alkaline non cyanide copper plating processes have been available as substitutes for the cyanide process. The obvious benefit is the elimination of cyanide from the wastewater stream. Not so obvious benefits include faster barrel plating speed, no cyanide in the F-006 waste from waste treatment (making delisting of the F-006 a more likely possibility), lower sludge volume generation due to lower metal concentrations, simplified wastewater treatment, no trouble with carbonate buildup, elimination or reduction from TRI (Toxic Release Inventory aka "Form R") reporting, and lower OSHA safety concerns.

While it is unlikely to happen on a frequent basis, if the cyanide copper solution ever requires disposal the cost is astronomical compared to the alkaline non cyanide process.

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Balancing the benefits are disadvantages such as:

Higer operating costs
Inability to use the process on zinc surfaces
(die castings and zincatedaluminum/magnesium)
Greater sensitivity to impurities
A chemistry that is more difficult to control

At least one of the non cyanide processes utilizes a "purification" cell in addition to the normal plating tank.

PROCESS DIFFERENCES:

ANCC	CC
No Cyanide	Cyanide
pH 8.8-9.8	pH 10.5-14+
Zinc Die Castings???	!!!!
Faster	Slower
Purification Cell	No Cell
Filtration	Optional
Impurity Sensitive	Not Sensitive
Control Problems	No Problem
Excellent Cleaning Req.	Not Req.
Constant Dummying	Not Req.
Special Anodes	Not Req.

Process Differences

The non cyanide process operates at a pH range of 8.8-9.8 while the full strength cyanide process is at pH 13-14 (cyanide strike baths for zinc die castings operate at pH 10-10.5). Despite the lower pH of the non cyanide process vs the cyanide process, the non-cyanide bath has trouble tolerating zinc contamination and has not been highly successful at depositing copper over zinc surfaces. Further research is presently under way to improve on this drawback (and also to develop a non cyanide brass). Both cyanide and alkaline non-cyanide copper processes operate at temperatures ranging 140-160 deg. F. The throwing power of the non cyanide process is superior to the cyanide process. This is especially evident in barrel plating. The non cyanide process utilizes cupric copper ions while the cyanide contains monovalent copper. This translates to faster plating at the same current density for the cyanide process. However, the non cyanide process can operate at higher current densities to yield faster plating overall. Changing over to the non cyanide process requires a lined tank and purification compartment outside the plating tank (for at least one of the commercial processes). Good filtration and carbon treatment are mandatory for the non cyanide process, not mandatory for the cyanide process. The cyanide process is more tolerant of poor cleaning practices, while the non cyanide process requires excellent cleaning prior to plating. The non cyanide processes use air agitation and at least one of them uses a purification cell with proprietary anodes that prevent accumulation of too much cuprous copper, while the cyanide process has no such requirement.

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DEPOSIT DIFFERENCES:	
ANCC	CC
Fine Grained	Fine Grained
Less Pure	Pure
Dense	Dense

Deposit Differences

Both types of copper plating baths yield a fine grained, dense deposit of equal metallurgical property, with the possible exception of purity, since the non cyanide process incorporates a trace of organic into the deposit from the additives. An ideal application for the non-cyanide process is for thick deposits used as heat treating (carburizing) stop-off on steel parts. The dense deposit is an excellent diffusion barrier for carbon.

POLLUTION PREVENTION:	
ANCC	CC
Recovery Possible	Also
Less Copper	More
Easy Waste Trt.	Harder
No CN-F006	CN-F006
Short Life	Long Life

Pollution Prevention

The cyanide and alkaline non-cyanide process function at elevated temperature, making recovery through drag-out control and other recovery systems viable. The non cyanide process contains 1/2 to 1/4 as much copper as a full strength cyanide copper bath, translating to lower sludge generation. Waste treatment is accomplished by pH adjustment with lime, or magnesium hydroxide, eliminating the two stage chlorination system from the waste treatment system and eliminating use of more dangerous chemicals such as chlorine or sodium hypochlorite. A potential negative pollution prevention effect would occur if the non cyanide bath frequently became contaminated beyond control (as happened during pilot scale testing in one case). The bath would then require treatment/disposal. Much of the copper could be recovered through electrolysis prior to such disposal, however.

Cyanide based copper plating solutions are far more tolerant of impurities and can last many years before requiring treatment/disposal. In fact, there are baths that are 30 years old or older out there!

The non cyanide process does not create a cyanide bearing F-006 waste. If copper

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plating on steel is the only source of cyanide in the F-006 waste, substitution of the non cyanide process may create a waste that qualifies for "delisting". EPA could help by promulgating a rule exempting waste from the treatment of rinsewater from alkaline non-cyanide plating as they did for non cyanide zinc plating (on ferrous substrates). Elimination of cyanide is one less TRI report also (but copper/copper compounds would still be reportable).

WORKER SAFETY/ECONOMICS:

ANCC	CC
No Cyanide	Cyanide
No Chlorine	Chlorine
No Ozone	Ozone
No Caustic	Caustic
More Expensive	Up to 1/3 Less

Worker Safety/Economics

The non-cyanide process offers an obvious advantage in worker safety by the elimination of cyanide. Cyanide catastrophes caused by accidental acidification of cyanide bearing solutions would be eliminated. Cyanide oxidants such as chlorine, hypochlorite and ozone would also be eliminated or reduced in usage. The lower alkalinity of the non cyanide process offers less concern about caustic burns.

Platers using the cyanide based process, with waste treatment systems currently in place for adequate treatment, currently have a decided competitive advantage based on economics. As the cost of waste treatment/disposal increases in the future and added pressure to reduce the publics' exposure to chemical catastrophes is created, more platers will chose the non cyanide process. The additional demand for the process may eventually result in lower costs. Some of the economic advantage of cyanide copper processes could be reduced if EPA granted F-006 waste from non-cyanide copper plating a RCRA exemption.

PROCESS DIFFERENCES:

NICKEL	COPPER
High Metal Content	Much Lower
Ammonium Ions	No
Cleaning Important	Not As Much
Hard To Control	Easier
Dummying* Req.	No

*Dummying=Low Current Density Electrolysis

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High pH Nickel for Copper Strike

High pH nickel plating solutions have been available for a long time as a substitute for copper strike on zincated surfaces and zinc die castings. Cyanide copper has fewer cleaning and analytical requirements and has therefore been favored to the point of elimination of the nickel process from consideration. The nickel process deserves a new look in light of the modern era of environmental concern.

Process Differences

Typical formulation/operating conditions for the nickel process are:

Nickel Sulfate: 10-15 oz/gal
Ammonium Chloride: 2-5 oz/gal
Sodium Sulfate (Anh): 10-15 oz/gal
Boric Acid: 2-3 oz/gal
pH: 5.3-5.8
Temperature: 70-90 deg. F
Current Density: 12-36 ASF

To obtain optimum results, the plater must balance the ratio between the nickel sulfate and the sodium sulfate. Complex shaped parts require higher sodium sulfate concentrations are employed. For operation above pH 5.4 ammonium hydroxide and sulfuric acid are used for pH control. At the lower pH range, sodium hydroxide and hydrochloric acid are used. Zinc contamination should be continuously removed through low current density dummying in a purification cell. Cleaning prior to plating would be more critical than for cyanide plating and equal to the effort for alkaline non-cyanide. Since the bath chemistry is not proprietary and there are no "additives" to purchase, the cost of operating this bath would be expected to be less than for operating the cyanide copper plating process and much less than operating the alkaline non cyanide process. The process has been used successfully to plate zincated aluminum and zinc die castings in the past.

DEPOSIT DIFFERENCES:

NICKEL	COPPER
Brittle	Soft
Poor Fatigue Strength	Strong
Porous	Dense
Passivation Problems	No

Deposit Differences

The higher the sodium content of this nickel plating bath, the more brittle the deposit becomes. The bath should therefore be used only as a "strike" before conventional nickel plating. Parts that undergo fatigue cycles or extreme temperature changes may experience early fatigue failures and less corrosion resistance.

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POLLUTION PREVENTION:	
NICKEL	COPPER
No Cyanide	Cyanide
Cancer	No
Ammonium	No
More Sludge	Less
No CN-F006	Cn-F006

Pollution Prevention
Substituting nickel plating for cyanide copper eliminates cyanide from the rinsewater, thereby yielding many of the pollution prevention benefits outlined for alkaline non cyanide copper. The ammonium ion may cause waste treatment problems unless its' concentration is minimized through drag-out recovery techniques. This bath contains a higher metal content than the cyanide copper process and twice the metal content as the alkaline non-cyanide process. Sludge volume from wastewater treatment would be affected accordingly.

WORKER SAFETY/ECONOMICS:	
NICKEL	COPPER
Lower Toxicity	Higher
Carcinogen	No
Nickel Itch	No
No "Catastrophe"	Possible
Cheap	More Expensive

Worker Safety/Competition
Since the bath operates at low temperatures, no ventilation would be required to control emissions to workers' air. Nickel plating salts are far less toxic than cyanide, but they have been tagged as suspected carcinogens and are on many companies' list for use reduction. Overall safety to workers would be improved and probability of a catastrophic accident would be eliminated when compared to cyanide copper. Worker safety level would not be as good as obtained with alkaline non cyanide copper.

Plants using the high pH nickel process would be expected to have a favorable economic advantage over plants with the alkaline non cyanide process and would have a slight edge on plants with the cyanide copper process, if analytical and waste treatment controls are kept under control.

Acid Salts for Hydrochloric Acid
Acid salts have a potential for replacing hydrochloric acid as a pre-dip prior to most plating processes. Acid salts (Sodium, hydrogen, sulfate aka sodium bisulfate) are a

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crystalline material that is easily handled and less dangerous to store (no liquid spills).

PROCESS DIFFERENCES:	
ACID SALTS	HYDROCHLORIC ACID
Powder	Liquid
No Smoke	Old Smokey
Weaker	Stronger
Little Attack On Subst.	Attack

Process Differences

Acid salts are relatively mild and can not readily dissolve significant amounts of rust. They presently find their greatest use in applications where a minor amount of de-rusting and alkali neutralization is needed. However, through augmentation by either elevating the temperature or adding cathodic power or both, the same benefits can be obtained from acid salts as would be from hydrochloric acid. Hydrochloric acid has the advantage of rapidly dissolving rust/corrosion products and having a greater capacity for alkali neutralization. The acid salts do not rapidly attack metals, while hydrochloric acid does.

POLLUTION PREVENTION:	
ACID SALTS	HYDROCHLORIC ACID
No TRI	TRI
Less Sludge	More
No Scrubbing	Scrubbing
Less Corrosion	Corrosion
Shorter Life	Longer Life

Pollution Prevention

Acid salts are not reportable under present TRI requirements. Because the attack on the base metal is less severe, less base metal enters the rinsewater stream, resulting in the generation of less sludge volume. Note: if the base metal is ferrous, less iron in the sludge may "concentrate" artificially other metals in the sludge, yielding a negative benefit. Hydrochloric acid requires ventilation and in most cases scrubbing of exhaust fumes, while acid salts do not (unless electrolyzed during use). Scrubbing of exhaust fumes generates additional waste requiring treatment. Hydrochloric acid is very corrosive to the surrounding hardware such as tanks, piping, and structural supports. Acid salts are less corrosive. Acid salts must be changed more frequently, since they are weaker, so storage capacity for spent acid must be increased in the waste treatment system.

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WORKER SAFETY/ECONOMICS	
ACID SALTS	HYDROCHLORIC ACID
Less Skin Attack	More
No Spill Problem	Spill Problem
No Splash Problem	Splash Problem
Easy Clean-up	Hard
Expense Same as HCL	

Worker Safety/Economics

Acid salts are far safer to handle than hydrochloric acid. When added to water, acid salts may yield a sharp odor, but do not create voluminous white clouds of acidic fumes. Worker safety is significantly improved. Spills of acid salts can readily be cleaned up, while hydrochloric acid spills can be major disasters.

Metal finishers who are presently equipped to use hydrochloric acid with proper environmental controls may have a slight economic advantage over those who would require an acid salt solution that needs heating and or electrification. Intangible or difficult to calculate cost savings such as improved worker safety and no TRI reporting could tip the balance in favor of acid salts having the competitive advantage.

Zinc Alloy Processes for Cadmium Plating

When cadmium electroplate is used mostly for enhanced corrosion resistance to salty environments, zinc alloy processes are suitable candidates as substitutes. Even pure zinc is a suitable substitute for heavy cadmium deposits (more than 1 mil). When cadmium is specified for enhanced lubricity, solderability, low electrical contact resistance, ease of disassembly after corrosion has occurred, or to obtain benefits from the toxicity of cadmium (organisms such as fungus or mold won't grow on it), zinc alloy deposits may fail to be suitable substitutes.

While non cyanide cadmium processes are presently commercially available, the most desirable substitute for a cadmium plating process would do away with both cyanide and cadmium, so we will focus on such substitutes only.

PROCESS DIFFERENCES:	
ZINC/ALLOY	CADMIUM
No Cyanide	Cyanide
Hard To Control	Easier
Cleaning Critical	No
Low Metal	High
Variety of Baths	No

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Process Differences

There presently are numerous zinc alloy processes commercially available, including zinc-cobalt, zinc-nickel, zinc-tin, and zinc-iron. The corrosion resistance obtained from these alloys stems from the addition of a more noble metal than zinc in the alloy thereby reducing the activity of the metallic coating while maintaining the cathodic nature of the coating for a steel substrate. Since there are many different processes available, we will present only an overview of the differences. Whenever a single metal process is replaced with a multi-metallic process, analytical control of the plating solution becomes far more critical. If the more noble metal content in the alloy exceeds a certain amount, chromating problems result. A wide variety of variables must be controlled to obtain the "right" alloy composition, often including pH, temperature, chemistry, and agitation level.

Zinc-nickel alloys can be plated from a chloride based process similar to chloride zinc baths or from an alkaline process similar to alkaline non cyanide zinc. Brightening agents and other additives make the alloy processes more expensive to purchase and operate than cyanide cadmium baths. The alloying metal is usually added as a chemical concentrate that is purchased from the supplier. This allows for the use of zinc anodes, since alloy anodes are not readily available or usable.

Cadmium can be plated from alkaline-cyanide, acid-non cyanide, neutral sulfate, and acid sulfate chemistries. The alkaline cyanide bath contains from 20 to 36 g/L of cadmium metal and as much as 150 g/L sodium cyanide. The neutral sulfate bath contains 4-10 g/L cadmium metal, but also contains up to 100 g/L of ammonium sulfate, yielding wastewater treatment problems. The acid sulfate contains up to 10 g/L of cadmium metal, the balance of the bath is made of 35 g/L sulfuric acid and additives. Cadmium can also be plated from a fluoborate chemistry, but the ingredients are expensive and the bath has poor throwing power.

DEPOSIT DIFFERENCES

ZINC/ALLOY	CADMIUM
Fine Grained	Yes
Soft/Harder	Soft
Non Toxic	Toxic
Hard To Solder (except tin-zinc)	Easy
Stress Corr. Cracking	No
Good Adhesion	Better

Deposit Differences

Zinc alloy deposits are fine grained, and generally harder than cadmium or pure zinc. Yellow chromates of the zinc alloys may have a significantly different appearance from pure zinc. For example zinc-nickel may look purple when chromated. The zinc-nickel and zinc-cobalt deposits can be very bright while the zinc iron and zinc-tin are less so. Solderability is marginal for all but the zinc-tin alloy. Zinc alloy deposits are much harder

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than cadmium and offer far less lubricity in torque tension applications, with the impossible exception of zinc-tin.Cadmium has a fine grained structure that offers excellent torque-tension properties (lubricity). Cadmium metal is toxic, so organisms such as mold and fungus will not grow on cadmium plated surfaces. Corrosion products of cadmium tend to readily break apart, while zinc and zinc-alloy corrosion products tend to hold fast.
A recent study, made the following conclusions after comparing a large number of environmentally acceptable substitutes (cyanide zinc was therefore omitted) to cadmium (from the cyanide chemistry) in real-life outdoor exposure:

a. Corrosion Resistance
Cadmium, Ion Vapor Deposited Aluminum/topcoat, Zinc (alkaline process), Zinc (chloride process), Zinc-Nickel (7-9% nickel) proved to be most effective corrosion protectors of steel in natural marine, industrial, and rural atmospheres. Contrary to popular thought, cadmium and zinc appeared to perform equally well in all three environments, including marine exposure.

b. Torque-Tension
Cadmium, A proprietary calcium carbonate/sulfonate emulsion, water based zinc coating, IVD Aluminum/Topcoat, Tin-Zinc, Zinc (alkaline process), Zinc (chloride process), and Zinc-Nickel exhibited the lowest disassembly breaking torques.

c. Environmentally Assisted Cracking (EAC)
Cadmium was found to be the least likely coating to promote EAC (aka stress corrosion cracking). The others all enhanced the susceptibility of high strength steel towards EAC, with zinc-nickel and tin-zinc yielding the best performance of the alternates. The two environments used in the experiment were 3.5% salt and oil/air.

d. Adhesion
The only plated coating to match the adhesion of cadmium was tin-zinc. The next best plated coating was zinc-nickel.

POLLUTION PREVENTION	
ZINC/ALLOY	CADMIUM
No Cyanide	Cyanide
Easy Waste Treat	Hard
No TRI	TRI
Easy Limits	Hard (.07mg/L)

Pollution Prevention
The zinc alloy processes offer the potential of eliminating two environmental hazards; cadmium and cyanide. Waste treatment is normally accomplished by simply adjusting pH,

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thereby eliminating the need for cyanide oxidation. Regulatory compliance would be easier to achieve since zinc and the alloying metal would have higher allowable discharge concentrations than those imposed on the cadmium process. The zinc-cobalt, zinc-tin, and zinc-iron processes do not add any metals that are presently regulated on the Federal level. The alloy processes are suitable for use with presently available recovery technologies, although recovery may pose increased chemical control problems. Substitution of a zinc alloy process for cadmium could remove another set of compounds that would normally be reportable under TRI reporting requirements.

WORKER SAFETY/ECONOMICS:

ZINC/ALLOY	CADMIUM
No Carcinogen (except zinc-nickel)	Carcinogen
Low Toxicity	High
Low Dermal Corrosion	High
Moderate Cost	Same

Worker Safety/Economics

By eliminating cadmium and cadmium compounds which are toxic and suspected as carcinogenic and by substituting a non cyanide process for one that typically contains high concentrations of cyanide, worker safety would be significantly improved. The economics of zinc-alloy plating depends on the process type chosen and its application. There may be a cost savings, if compliance problems are factored in. Unalloyed zinc plating will almost always be less expensive than cadmium.

Nickel-Tungsten-Silicon Carbide for Hard Chromium

This coating consists of a nickel-tungsten alloy deposit with silicon carbide particles dispersed throughout the coating. The chemistry was patented by Takata in 1990 and is currently under consideration by several large manufacturing companies as a substitute for hard chromium.

PROCESS DIFFERENCES

Ni-W-SiC	CHROMIUM
pH 6-8	pH approx 3
175°F	140°F
Current Density = 24-35 Adm^2	Current Density = 10-25 Adm^2

Process Differences

The alloy/dispersion coating contains nickel sulfate (35 g/L), sodium tungstate (65 g/L), and ammonium citrate (110 g/L). Fine silicon carbide particles (30 g/L) are suspended

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within the plating bath by continuous agitation. The silicon carbide particles are incorporated into the deposit as it forms. The bath operates at pH 6-8 and is adjusted with ammonium hydroxide or citric acid. Bath temperature is 150-175 deg. F. Plating current density is 100-300 ASF. The hexavalent chromium chemistry contains chromium trioxide (250 g/L) and a trace amount of sulfuric acid (2.5 g/L) or sulfuric acid (1.2g/L) and a fluoride containing compound, yielding a fluoride ion strength of about 1 g/L. It typically operates at 120-140 degrees F and at 150-300 ASF.
The alloy process can deposit the same thickness in half the time compared to a conventional hard chromium process due to current efficiencies of 24-35% vs 10-12% for conventional baths (one commercial chromium process operates at 25% current efficiency and would therefore match the alloy plating speed). The alloy process has significantly better throwing power, although complicated shapes still require auxiliary anodes.
There presently is no good technique for stripping the alloy process, or performing "spot repairs" while the chromium process is easily stripped and some parts can be spot plated. The alloy process is sensitive to metallic contamination, while the chromium process is very tolerant. Because the alloy process utilizes citrates at relatively neutral pH, it is subject to biological activity such as mold/bacteria growth.

The alloy process utilizes a tungsten compound that is very expensive and difficult to obtain. Some companies investigating the process have resorted to producing their own sodium tungstate from other tungsten compounds.

DEPOSIT DIFFERENCES:

Ni-W-SiC	CHROMIUM
Softer	Harder
Better Wear	Excellent Wear
Less Corr. Res.	Better
Less Hydrogen	More

Deposit Differences
The nickel tungsten alloy has a slightly lower hardness when compared o chromium. The wear resistance of the alloy is enhanced by the silicon carbide matrix which far exceeds the hardness of chromium. The alloy performs better in abrasive wear applications than chromium when tested with a Taber abrasion apparatus.

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POLLUTION PREVENTION:	
Ni-W-SiC	CHROMIUM
No Cr	Cr
W, Ni	No Ni, W
Waste Trt. Prob.	No Problem
Low Disaster Haz	Haz
Less Sludge	More
Recoverable	Recoverable
Possible Short Life	Long Life

Pollution Prevention

Substitution of a hard chromium plating solution eliminates hexavalent chromium from the wastewater and air discharges of metal finishing facility. However, the alloy process utilizes nickel and tungsten compounds which have also been linked to cancer. The net effect is to replace one carcinogenic material with two that are possibly lesser . Since the plating efficiency of the alloy process is only 24-35%, the process requires exhaust and scrubbing to reduce air emissions. Air emissions regulations of nickel will most likely be regulated under the Clean Air Act. EPA presently has no plans to regulate tungsten emissions because little or no tungsten is currently used by the metal finishing industry. Should the alloy process become popular, we would expect tungsten limitations on air, water and land (RCRA) emissions. High concentrations of ammonium ions in the wastewater stream would cause serious wastewater treatment problems due to chelation of metals such as copper and nickel. None of the ingredients in the alloy bath is an oxidant, so storage of the chemicals is simplified and the hazards of unwanted reactions and explosions caused by accidental combination of oxidizer and reducing agent is eliminated.

WORKER SAFETY/ECONOMICS:	
Ni-W-SiC	CHROMIUM
Draw????	
$$$$$	$

Worker Safety/Economics

Worker safety is not significantly improved by the substitution of Ni-W-Si for chromium. While hexavalent chromium is toxic and carcinogenic, nickel is also considered toxic and carcinogenic. Tungsten compounds are listed as teratogens (birth defects).

Economic data on nickel-tungsten-silicon carbide is not available at this time. Considering the difficulty in obtaining tungsten containing chemicals, it would be safe to assume the cost would be much higher than for chromium plating.

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Carbon for Electroless Copper

The circuit board industry is looking at a proprietary process that produces conductivity in the thru-holes with carbon. The process uses conventional plating equipment and reduces the number of processing tanks it takes to produce plated thru-holes. The process also would eliminate the use of formaldehyde, which is a suspected carcinogen.

PROCESS DIFFERENCES:

CARBON	E'LESS COPPER
Prop. Conditioner	No
Prop. Cleaner	No
Alkaline	Also
Fine Carbon	Formaldehyde
(0.15 micron)	and Copper

Process Differences

The printed circuit boards are prepared prior to carbon coating in the same manner as for electroless copper, including etch-back. Immediately prior to carbon coating, the boards are processed through a proprietary cleaner and proprietary conditioning solutions which are alkaline and contain weak complexing agents. The carbon coating solution is also slightly alkaline and contains extremely fine carbon particles on the order of .15-.25 microns (6-10 millionths of an inch). The process has been commercially available since 1989 and is presently in use by many circuit board facilities. Suitability for plating on plastics is unknown.

DEPOSIT DIFFERENCES:

CARBON	E'LESS COPPER
Thin Carbon Ctng.	Thin Copper Ctng.
Good Adhesion	Same
Good Therm Exp.	Same

Deposit Differences

The carbon adsorbed onto the clean/etched surface of the circuit board can yield a conductive surface that when copper plated compares favorably with electroless copper in adhesive strength and thermal expansion characteristics. MIL-P-55110D permits the use of this technology as a substitute for electroless copper.

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POLLUTION PREVENTION:	
CARBON	E'LESS COPPER
No Chelates	Chelates
No Formaldehyde	Formaldehyde
No Heavy Metal	Heavy Metal
Possible WT Prob.	Also
Inc. COD	Possibly same
Organic Collector	No

Pollution Prevention/Regulatory Impact

Elimination of electroless copper removes a heavily chelated process from the wastewater stream and at the same time, eliminates a carcinogenic material (formaldehyde) from use in the shop. While it is unlikely to happen, finely divided carbon can react violently if contacted with a strong oxidizer such as chromic acid. The suspended carbon may also cause problems in wastewater treatment, by coating over probes, clogging filters, and interfering with the proper operation of a clarifier. The carbon will not be removed by conventional precipitation systems and needs to be controlled at the source. Carbon in the wastewater discharge will significantly increase COD loading to the POTW. The carbon may also act as an organic "collector", increasing Total Toxic Organic concentrations in the wastewater discharge. Some POTWs have "excessive coloration" regulations. Carbon containing discharges would probably fail to meet such regulations. Plants using the carbon process and successfully controlling the above problems will reduce the amount of solid/liquid waste generated.

WORKER SAFETY/ECONOMICS:	
CARBON	E'LESS COPPER
No Carcinogen	Formaldehyde
Economics may be a draw	

Worker Safety/Economics

Worker safety would be significantly improved by the elimination of formaldehyde from the plating process.

Competitors using this process may have a competitive advantage by not have to waste treat complexed copper by not using activation processes that contain palladium and tin and by not generating as much solid waste for disposal. Added equipment for dealing with the finely divided carbon may neutralize this economic advantage, however.

End Chapter 5

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Appendix To Chapter V
Some Chemicals Used in the Metal Finishing Industry

Chemical	pH adjustment required	Cyanide or chromium treatment required	Waste products
Aluminum potassium sulfate	X		MS, DS
Aluminum silicate	X		MS, DS
Ammonium acetate	X		DS, NH3
Ammonium bifluoridee	X		MS DS, NH3
Ammonium chloride	X		DS, NH3
Ammonium citrate	X		DS NH3, O
Ammonium hydroxide	X		DS, NH3
Ammonium molybdate	X		MS, DS, NH3
Ammonium nitrate	X		K, NH3
Ammonium sulfate	X		MS, DS, NH3
Anisic aldehyde	X		O
Antimony potassium tartrate	X		MS, DS, O
Barium carbonate	X		MS
Barium sulfate	X		MS
Benzene (benzol)	X		O
Boric acid	X		DS
Cadmium cyanide		X	MS, DS
Cadmium sulfate	X		MS, DS
Calcium nitrate	X		DS
Chromic acid		X	MS, DS
Citric acid	X		DS,O
Cobalt carbonate	X		MS
Cobalt sulfate	X		MS, DS
Cupric sulfate	X		MS, DS
Diammonium phosphate	X		MS, DS, NH3
Ferric nitrate	X		MS, DS
Fluoboric acid	X		MS, DS
Formaldehyde	X		O
Glue			O
Glycerine	X		O
Hydrazine sulfate	X		DS
Hydrochloric acid CP	X		DS
Hydrofluosilicic	X		MS, DS
Hydrogen peroxide	X		

Chemical	pH adjustment required	Cyanide or chromium treatment required	Waste products
Hydroxyacetic acid	X		DS, O
Hypophosphorus acid	X		MS, DS
Indium sulfate	X		MS,DS
Iron oxide	X		MS
Isopropanol	X		O
Lard Oil			O
Lead Fluoborate	X		MS,DS
Lead oxide	X		MS
Lime (calcium hydroxide)	X		MS
Magnesium sulfate	X		MS, DS
Manganese carbonate	X		MS
Manganese sulfate	X		MS, DS
Methanol	X		O
Monoammonium phosphate	X		MS, DS, NH3
Nickel carbonate	X		MS
Nickel chloride	X		MS, DS
Nickel sulfate	X		MS, DS
Nickel sulfamate	X		MS, DS
Nitric Acid	X		DS
Oxalic acid	X		MS, DS
Phosphorus acid	X		MS, DS
Potasium bromate	X		DS
Potassium citrate	X		DS,O
Potassium chloride	X		DS
Potassium copper cyanide		X	MS, DS
Potassium cyanide		X	MS, DS
Potassium ferricyanide		X	MS, DS
Potassium hydroxide	X		DS
Potassium phosphate	X		DS
Potassium stannate	X		MS,DS
Potassium thiocyanate	X		DS
Sodium acid pyrophosphate	X		MS, DS
Soda ash (sodium carbonate)	X		DS
Sodium bicarbonate	X		DS
Sodium bisulfite	X		DS
Sodium bifluoride	X		MS, DS
Sodium citrate	X		DS,O
Sodium copper cyanide		X	MS, DS

Chemical	pH adjustment required	Cyanide or chromium treatment required	Waste products
Sodium cyanide		X	DS
Sodium dichromate		X	MS, DS
Sodium fluoborate		X	MS, DS
Sodium gluconate		X	DS
Sodium hexametaphosphate	X		MS, DS
Sodium hypophosphite	X		MS, DS
Sodium Hydrosulfite	X		DS
Sodium hydroxide (caustic soda)	X		DS
Sodium metasilicate	X		MS, DS
Sodium molybdate	X		MS, DS
Sodium nitrate	X		DS
Sodium orthosilicate	X		MS,DS
Sodium polysulfide	X		MS, DS
Sodium stannate	X		MS, DS
Sodium sulfate	X		DS
Sodium sulfide	X		MS,DS
Sodium sulfite	X		DS
Sodium tripolyphosphate	X		MS, DS
Stannous fluoborate	X		MS, DS
Stannous sulfate	X		MS, DS
Stearic acid	X		O
Sulfamic acid	X		DS
Sulfur (Liquid)	X		MS
Sulfuric acid	X		MS, DS
Tallow glvceride	X		O
Tartaric acid	X		O
Tetrapotassium pyrophosphate	X		MS, DS
Tetrasodium pyrophosphate	X		MS,DS
Toluene (Toluol)			O
Trichlorethylene			O
Trichloroethane			O
Trisodium phosphate	X		MS, DS
Xylene (Xylol)			O
Zinc chloride	X		MS,DS
Zinc cyanide		X	MS, DS

MS = metal sludge; NH3 = ammonia; DS = dissolved solids; O = organic matter.

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Part VI, KEY DRIVERS AND BARRIERS TO POLLUTION PREVENTION IN METAL FINISHING

Tier 1: Top Firms, pride in industry
Tier 2: Maintain regulatory compliance
Tier 3: Older outdated facilities
Tier 4: Renegade, non-compliance

Inconsistency due to uncertainty

A recent survey conducted by USEPA concluded that drivers and barriers to pollution prevention vary for different "tiers" in the metal finishing industry:

Tier 1: These are top firms, driven by recognition and pride in industry performance. They see the economic payoffs of strategic environmental investments. They maximize flexibility in compliance and promote innovative approaches and willingness to share knowledge in pollution prevention methods.

Tier 2: These firms are driven mainly by the need to maintain regulatory compliance. Barrier to pro-active performance include lack of capital, information, positive reenforcement, and a non-level playing field created by lack of uniform enforcement on their competitors. Many facilities at this level are heavily dependent upon their suppliers for methods of pollution prevention.

Tier 3: These are older, outdated facilities that have a strong fear of liability under Environmental regulations and find it difficult to improve due to lack of capital, knowledge, and floor space.

Tier 4: These are "renegade" facilities that compete at an unfair advantage gained through non-compliance with environmental regulations. The facilities may be "hidden" and un-reported, or may be going through an appearance of compliance.

Inconsistency among regulatory requirements and enforcement actions at federal, state, and local levels creates a major barrier in advancing pollution prevention, due to the "uncertainty" factor about upcoming or modified regulations that might render a major investment unusable or problematic. Uncertainty also makes long range planning difficult or impossible.

Some regulatory provisions are in themselves significant barriers to pollution prevention in this industry:

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Listing of Hazardous Waste

* F-006 RCRA, 40 CFR part 261
* Need viable method of proving non-hazardous status

Mixture/Derived From Rule

* RCRA, 40CFR part 261.3 (a) (2) (iv)
* Inhibits recycling of hazardous waste

Listing of Hazardous Waste (F-006) (RCRA, 40CFR part 261)

The waste generated from the wastewater pretreatment system from an electroplating operation is a hazardous waste due to listing (there are very few exemptions, such as waste from pretreatment of rinsewater from non-cyanide zinc electroplating on ferrous substrates). There are provisions in the regulations for "delisting" a hazardous waste, but the procedures are extremely expensive and time consuming. The generated waste, in many cases, would not meet the listing criteria and theoretically would meet non-hazardous status, if EPA created a procedure for determining whether a metal finishing waste meets the listing criteria. Until such time occurs, metal finishing facilities appear to be generating large volume of "hazardous" waste simply because no viable method of proving its non-hazardous status is available.

Mixture/Derived From Rule (RCRA, 40CFR part 261.3 (a) (2) (iv))

This provision of the RCRA regulations effectively causes any mixture of hazardous waste with non-hazardous materials to be come a hazardous waste in total. Further, any material **derived** from a hazardous waste is also considered hazardous. Even if the waste or product derived from the waste is treated or is inherently non-hazardous, there is no "out". This provision has been successfully challenged in court, but EPA is enforcing it on an interim basis, while it seeks to develop methods of defining a hazardous waste. In the meantime, this RCRA provision inhibits recycling of hazardous waste, except by a few companies who have spent the large sums of money necessary to "delist" their by products from recycled hazardous waste. It also drives the cost of disposing recyclable waste up and creates recycling opportunities only for the facilities that can afford to send the waste to such recycling firms (all of which are located outside the state of Illinois, except for one facility, Recontek, located in Illinois, but very limited in capability.

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Metal Finishing Standards (CWA, 40CFR part 433)

In the promulgation of the metal finishing standards, EPA stated their intent to move existing job shop electroplaters from 40CFR part 413 regulation to regulation under part 433. The difference between the two standards is significant:

PRETREATMENT STANDARDS (mg/L)

	Job Shops:		Metal Finishers:	
Pollutant:	1 Day Max	4 Day Avg	1 Day Max	30 Day Avg
Cadmium	1.2	0.7	0.69*	0.26*
Chromium	7.0	4.0	2.77	1.71
Copper	4.5	2.7	3.38	2.07
Lead	0.6	0.4	0.69	0.43
Nickel	4.1	2.6	2.61	1.48
Silver	----	----	0.43	0.24
Zinc	4.2	2.6	2.61	1.48
Cyanide-T	1.9	1.0	1.2	0.65
TTO	2.13 (grab)		2.13 (grab)	
pH	----	----	6-9	6-9
Cu + Zn + Cr + Ni (Total Metals)	10.5	6.8	----	----

Above are the most commonly applied sewer discharge regulations. Note that job shops have in general, higher limitations than metal finishers. *

We should also note that new source metal finishers must meet regulated Cadmium discharge levels at 0.11mg/L 1 Day max and 0.07 mg/L 30 Day Avg. Also, the cyanide limits for metal finishers must be complied with a**t the point of treatment** (as opposed to the end of pipe for job shop metal finishers).

An existing job shop electroplating facility risks the re-classification into new source metal finishing category, if it invests the money necessary to relocate, or to tear down an older processing line and replace it with a modern line incorporating modern pollution prevention methods.

In several cities, POTWs have interpreted major renovations to pretreatment systems as sufficient modernization to re-classify the shop in the metal finishing category!

Such misinterpretations of the intent of the federal regulations are counterproductive, as an existing facility will tend to resist modernizing, in an effort to maintain their existing discharge category.
Federal guidance as to what constitutes enough change to re-categorize a facility is needed.

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Superfund, Joint and Several Liability Provisions

* Discontinue / liquidate
* Cautious Lenders
* Harmful Government Specs
* Break-in period - violations
* "Charlatan" saviors
* Cross media effects
* Hesitant attitude - history, knowledge

Superfund, Joint and Several Liability Provisions

A number of metal finishing firms face significant environmental liabilities and clean-up costs, if they discontinue operations and attempt to liquidate their assets. This potential liability creates the double "whammy" of creating a barrier to exit for these firms and effectively eliminating access to capital for improvements.

Liability provisions under Superfund, that hold lenders of capital liable, in the event of a Superfund clean-up at a metal finishing facility, causes lenders to be extremely cautious in providing necessary capital for metal finishers to improve their operations and install pollution prevention methods.

Other barriers to pollution prevention include:

The embarrassing tendency of governmental defense agencies to continue to specify environmentally harmful coatings to be applied to military components, even when less harmful alternates are available.

There is a concern about the "break-in" period that normally is required after a pollution prevention device or technique is installed. Invariably, the "learning curve" will cause a violation of a local or state regulation, as an operating parameter is refined or if the equipment breaks down. The resulting violation acts as a deterrent to the installation of the device.

The industry has seen many "charlatan" saviors, who profess to have all the answers in their little "black box". Poor experiences and lost capital expended on such devices has created an aura of suspicion about any new technology that enters the market.

Cross media effects can also inhibit pollution prevention, as when an improved method for scrubbing air emissions ends up creating more scrubbant waste to treat, and at higher concentrations than before.

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A considerable lack of history and control knowledge about substitute "cleaner" processes creates a hesitant attitude about investing in a substitute process.

There is considerable concern about recycling methods contaminating the process the recycling method is installed on, causing the entire process solution to be sent off site for treatment/disposal. It is not un-common for a metal finishing process solution to cost $15.00/gallon to make-up (some solutions are as high as $30.00/gal and precious metals plating solutions can cost thousands of dollars per gallon). By recycling rinsewater to such processes (as opposed to treating), the concern is that in the long term the recycling method will contaminate the process beyond salvageability and therefore create more waste than was saved.

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